American Water Works Association
RESEARCH FOUNDATION®

ADVANCING THE SCIENCE OF WATER

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MEMORANDUM

TO: Project Advisory Committee - Application of Bioreactor Systems to Low-concentration Perchlorate-Contaminated Water

Glen Boyd
John Carman
Robin Collins
Kevin Mayer

DATE: November 23, 1998

FROM: Frank J. Blaha, Project Manager

RE: Quality Assurance Project Plan Documents

At the time of Request for Proposals (RFPs) for the perchlorate projects, we included in the RFPs all of the requirements we were aware of at that time. However, there are some additional EPA requirements which we need to have addressed in our perchlorate projects that were not specifically identified in our RFPs.

These additional requirements are being made part of our contracts with the researchers as Attachment G. Attached is a copy of Attachment G, as well as three guidance documents from EPA on the preparation of Quality Assurance Project Plans (QAPPs). This guidance takes the form of two guidance documents for a Category IV QAPP document for basic research, and a single guidance document on a Category III QAPP for applied research (pilot studies). The QAPP is to be submitted to the EPA QA office as a separate document thirty days prior to the beginning of any measurement, data gathering, or data generation activity. The EPA has indicated they will probably be able to review these QAPP documents in less than thirty days. If EPA does review and approve these documents in less than thirty days, then data generation can start that much sooner.

We feel the PAC should be an integral part of the review of these QAPPs, even though EPA is ultimately responsible for "approving" them. Therefore, I am including a copy of the EPA guidance documents as well as a QAPP submission from Bruce Logan of Pennsylvania State University. Dr. Logan had made an earlier submission of a preliminary QAPP. I passed that document on to EPA, and passed EPA comments on to Dr. Logan. The intent was to get the document closer to complete and correct before sending it through the official channels of the contract. This is Dr. Logan's revised QAPP based on those earlier, preliminary, EPA comments. I would assume that this revised QAPP should be very close to meeting all of the EPA needs relative to QAPPs. Since these QAPP documents have not typically been a part of AWWARF agreements with EPA, AWWARF is also trying to establish a good understanding of the requirements and elements of these QAPPs.

This QAPP from Bruce Logan is for your review and comment. The EPA guidance documents are for your files and use in reviewing Dr. Logan's document. I would like to get any comments you might have on Dr. Logans's QAPP by next week Wednesday, December 2, 1998. This is a shorter review than will be typical for the other deliverables on this project, but I want to get this document into EPA's hands quickly, unless there are fatal flaws contained in this document.

If you have any questions, please call or email me. My phone is 303-347-6244, my fax number is 303-734-0196 and my Internet address is fblaha@awwarf.com.

FJB:dh:2530

Enclosures

Draft Attachment G
Category III Guidance
Category IV Guidance
Recent EPA QAPP Guidance (1998)
QAPP from Dr. Logan

Exhibit G

Project 2530

Application of Bioreactor Systems to Low-Concentration Perchlorate-Contaminated Water

Quality Assurance for Category III Projects (Applied Research Projects)

A. **Quality Assurance Project Plan (QAPP)** This project requires an EPA approved QAPP. The QAPP shall be submitted by the awardee to the AWWARF project manager. The QAPP shall be submitted to AWWARF in a timeframe that allows AWWARF to submit this to EPA thirty (30) days prior to the beginning of any measurement, data gathering, or data generation activity.

The awardee shall submit ten (10) copies of the QAPP to AWWARF, with five (5) copies intended for the EPA PO/WAM in order that the QAPP can be reviewed by the EPA technical/management staff in concert with its QA office, its QA support group, or an authorized representative of the Government. The awardee should also provide any supporting documentation, such as work plans, standard operating procedures, etc.

No measurement, data gathering, or data generation activity may be started without a completed EPA NRMRL-Ci Record of Approval/Non-approval for QAPPs documenting approval of the QAPP. (Deviations from having an approved QAPP will constitute a violation of EPA Order 5360)

The QAPP shall contain, in document control format, a thorough discussion of the awardee's and any subcontractor's internal quality assurance and quality control (QA/QC) procedures. It shall also contain provisions for the external review of the QA/QC program designed for the project.

Guidance on the development of a Category III QAPP is provided in the RREL Pocket Guide *Preparing Perfect Project Plans*, EPA/600/9-89/087, Oct. 1989. Additional guidance can be found in the document *Preparation Aids for the Development of Category III Quality Assurance Project Plans*, EPA/600/8-91/005, Feb. 1991. Both documents can be obtained from the EPA PO/WAM or by calling 513.569.7562 and requesting a free copy. The QAPP shall contain the following key elements as a minimum:

1. Project description, including the intended use of the data
2. QA objectives for critical measurements (i.e. process and analytical measurements essential to achieving project objectives) and the impact of not meeting the QA objectives
3. Site selection criteria (if applicable) and sampling procedures
4. Analytical Procedures (including instrument calibrations and frequency)
5. Data reduction, validation, and reporting
6. Internal quality control checks
7. Plans for performance and systems audits (as applicable)
8. Calculation of data quality indicators
9. Corrective action (criteria and procedures)
10. Quality Control reports to management

Following written approval of the QAPP by EPA, the awardee and any subcontractor shall implement the approved QAPP. Any substantive changes to the specifications in the approved QAPP shall be documented by the awardee as a revision to the QAPP. The awardee shall identify the change and explain the rationale for the change. The EPA, in concert with the awardee, is responsible for ensuring that the QAPP is kept current. Any

revisions to an approved QAPP must be submitted to the EPA PO/WAM and the QA office for review. Implementation of the revision(s) commences only after the awardee receives a copy of the EPA NRMRL-Ci Record of Approval/Non-approval for QAPPs documenting approval of the revision(s). (The term "substantive change" is defined as "any change in an activity that may alter the quality of data being generated or gathered".)

B. **Quality Assurance Audits** The awardee and any subcontractor shall anticipate that one or more quality assurance audits may be performed during the project duration. These external quality assurance audits will be performed by EPA or authorized Government personnel in concert with the EPA NRMRL-Ci QA office or support group. Selection of the specific areas of focus for audits will be commensurate with the scope and needs of the program. (Note: These external audits are intended to complement, not replace, the good laboratory practice of internal audits performed by the awardee.)

C. **Quality Assurance Reporting** Each interim or final report produced as a result of a measurement, data gathering or data generation activity shall include, as an integral section of the project report or as an Appendix, a readily identifiable discussion of the data quality of research results. Interim reports shall include the following items as a minimum:

Discussions of the quality of data produced in terms of precision, accuracy, completeness, method detection limit, representativeness, and comparability, or semi-quantitative assessments of data quality, as applicable.

- Changes to the QAPP, if any.
- Limitations or constraints on the use of the data, if any.
- Results of performance or systems audits.
- Identification of any significant QA/QC problems encountered.
- Resolution (i.e. corrective actions) of significant QA/QC problems.
- Discussions on the QA objectives that were met and those that were not.

The QA section of a project's final report should lend support to the credence of the data as well as the validity of the conclusions. Data quality statements for precision and accuracy shall be included.

The awardee shall comply with EPA's Chapter 5 document "Calculation of Precision, Bias, and Method Detection Limit for Chemical and Physical Measurements, March 30, 1984" whenever normally or near normally distributed data are assessed. When data normality cannot be confirmed or assessed then the awardee shall delineate the specific approach by which the data sets have been assessed.

D. **Ethics and Data Integrity** The awardee and any subcontractor shall adhere to an ethics and data integrity code. No person shall participate in:

- The intentional selective reporting of data,
- The intentional reporting of data values that are not the actual values obtained
- The intentional reporting of dates and times of data analyses that are not the actual dates and times of data analyses, or
- The intentional representation of another's work as one's own.

Quality Assurance for Category IV Projects (Basic Research Projects)

A. **Quality Assurance Project Plan (QAPP)** This project requires an EPA QAPP. The QAPP shall be submitted by the awardee to the AWWARF project manager. The QAPP shall be submitted to AWWARF in a timeframe that allows AWWARF to submit this to EPA thirty (30) days prior to the beginning of any measurement, data gathering, or data generation activity.

The awardee shall submit ten (10) copies of the QAPP to AWWARF, with five (5) copies intended for the EPA project officer/work assignment manager (PO/WAM) in order that the QAPP can be reviewed by the EPA technical/management staff in concert with its QA office, it QA support group, or an authorized representative of the government. The awardee should also provide any supporting documentation, such as work plans, standard operating procedures, etc.

No measurement, data gathering, or data generation activity may be started without a completed EPA NRMRL-Ci record of approval/non-approval for QAPPs documenting approval of the QAPP.(Deviations from having an approved QAPP will constitute a violation of EPA Order 5360)

The QAPP shall contain, in document control format, a thorough discussion of the awardee's and any subcontractor's internal quality assurance and quality control (QA/QC) procedures. It shall also contain provisions for the external review of the QA/QC program designed for the project.

Guidance on the development of a Category IV QAPP is provided in the RREL Pocket Guide *Preparing Perfect Project Plans* EPA /600/9-89/087, Oct. 1989. Additional guidance can be found in the document *Preparation Aids for the Development of Category IV Quality Assurance Project Plans*, EPA/600/8-91/006, Feb. 1991. Both documents can be obtained from the EPA PO/WAM or by calling 513.569.7562 and requesting a free copy. The QAPP shall contain the following key elements as a minimum:

- Project description, including the intended use of the data
- QA objectives for critical measurements (i.e., process and analytical measurements essential to achieving project objectives) and the impact of not meeting the QA objectives
- Sampling and analytical procedures
- Approach to QA/QC

Following written approval of the QAPP by EPA, the awardee and any subcontractor shall implement the approved QAPP. Any substantive changes to the specifications in the approved QAPP shall be documented by the awardee as a revision to the QAPP. The awardee shall identify the change and explain the rationale for the change. The EPA in concert with the awardee is responsible for ensuring that the QAPP is kept current. any revisions to an approved QAPP must be submitted to the EPA for review. Implementation of the revision(s) commences only after the awardee receives a copy of the EPA NRMRL-Ci Record of Approval/Non-approval for QAPPs documenting approval of the revision(s). (The term "substantive change" is defined as "any change in an activity that may alter the quality of data being generated or gathered".)

B. **Quality Assurance Audits** The awardee and any subcontractor shall anticipate that one or more quality assurance audits may be performed during the project duration. These external quality assurance audits will be performed by EPA or authorized government personnel in concert with the EPA NRMRL-Ci QA office or support group. Selection of the specific areas of focus for audits will be commensurate with the scope and needs of the program. (Note: These external audits are intended to complement, not replace, the good laboratory

practice of internal audits performed by the awardee.)

C. **Quality Assurance Reporting** Each interim or final report produced as a result of a measurement, data gathering or data generation activity shall include, as an integral section of the project report or as an Appendix, a readily identifiable discussion of the data quality of research results. Interim reports shall include the following items as a minimum:

- Discussions of the quality of data produced in terms of precision, accuracy, completeness, method detection limit, representativeness, and comparability, or semi-quantitative assessments of data quality as applicable.
- Changes to the QAPP, if any.
- Limitations or constraints on the use of the data, if any.
- Identification of any significant QA/QC problems.
- Resolution (i.e., corrective actions) of significant QA/QC problems.
- Discussions on the QA objectives that were met and those that were not.

The QA section of a project's final report should lend support to the credence of the data as well as the validity of the conclusions. Data quality statements for precision and accuracy shall be included.

The awardee shall comply with EPA's Chapter 5 document *Calculation of Precision, Bias, and Method Detection Limit for Chemical and Physical Measurements*, March 20, 1984, whenever normally or near normally distributed data are assessed. When data normality cannot be confirmed or assessed then the awardee shall delineate the specific approach by which the data sets have been assessed.

D. **Ethics and Data Integrity** The awardee and any subcontractor shall adhere to an ethics and data integrity code. No person shall participate in:

- The intentional selective reporting of data,
- The intentional reporting of data values that are not the actual values obtained,
- The intentional reporting of dates and times of data analyses that are not the actual dates and times of data analyses, or
- The intentional representation of another's work as one's own.

QAPP REQUIREMENTS FOR BASIC RESEARCH PROJECTS

A basic research project is typically defined as a study performed to generate data used to evaluate unproven theories, processes, or technologies. These studies are often bench-scale. The required documentation listed below may also be appropriate for other small-scale studies. The Divisional QA Manager should be consulted if necessary.

SECTION 0.0, APPROVAL BY PROJECT PARTICIPANTS

0.1 The EPA TLP shall be responsible for obtaining signatures of appropriate project participants on the project objective agreement (POA), documenting agreement to project objectives and the approach for evaluating these objectives.

SECTION 1.0, PROJECT DESCRIPTION, OBJECTIVES, AND ORGANIZATION

1.1 The purpose of study shall be clearly stated in the QAPP.

1.2 The process, site, facility, apparatus, and/or environmental system to be tested shall be fully described in the QAPP.

1.3 Project objectives shall be clearly stated in the QAPP and identified as being primary or non-primary.

1.4 Responsibilities of all project participants shall be identified in the QAPP, meaning that key personnel and their organizations shall be identified, along with the designation of responsibilities for planning, coordination, sample collection, measurements (i.e., analytical, physical, and process), data reduction, data validation(independent of data generation), data analysis, report preparation, and quality assurance.

SECTION 2.0, EXPERIMENTAL APPROACH

2.1 All known or pre-established test conditions and variables shall be provided in the QAPP.

2.2 All measurements (i.e., analytical [chemical, microbiological, assays,etc.], physical, and process) shall be identified for each sample type or process, and project-specific target analytes shall be listed and classified as critical or noncritical in the QAPP.

2.3 Sampling or monitoring points for all measurements (i.e., including locations, access

points, etc.,whenever applicable) shall be identified in the QAPP.

2.4 *For all known or pre-established test conditions, the frequency of sampling/monitoring, as well as the numbers for each sample type and/or location shall be provided, including QC and reserve samples.*

2.5 *The planned approach for evaluating project objectives (i.e., data analysis), including formulas, units, definitions of terms, and statistical analysis, if applicable, shall be included in the QAPP.*

SECTION 3.0, SAMPLING PROCEDURES

3.1 *Whenever applicable or necessary to achieve project objectives, the method used to establish steady-state conditions shall be described in the QAPP,*

3.2 *Each sampling/monitoring procedure to be used shall be described in detail or referenced in the QAPP. If compositing or splitting samples, those procedures shall be described in the QAPP.*

3.3 *Sampling/monitoring procedures shall be appropriate for the matrix/analyte being tested.*

3.4 *If sampling/monitoring equipment is used to collect critical measurement data (i.e., used to calculate the final concentration of a critical parameter), the QAPP shall describe how the sampling equipment is calibrated.*

3.5 *If sampling/monitoring equipment is used to collect critical measurement data, the QAPP shall describe how cross-contamination between samples is avoided.*

3.6 *When representativeness is essential for meeting a primary project objective, the QAPP shall include a discussion of the procedures to be used to assure that representative samples are collected.*

3.7 *A list of sample quantities to be collected, and the sample amount required for each analysis, including QC sample analysis, shall be specified in the QAPP.*

3.8 *Containers used for sample collection for each sample type shall be described in the QAPP.*

3.9 *Sample preservation methods (e.g., refrigeration, acidification, etc.), shall be described in the QAPP.*

3.10 *Holding time requirements shall be noted in the QAPP.*

SECTION 4.0, TESTING AND MEASUREMENT PROTOCOLS

4.1 Each measurement method to be used shall be described in detail or referenced in the QAPP. Modifications to EPA-approved or to similarly validated methods shall be specified.

4.2 Methods shall be appropriate for the matrix/analyte being tested.

4.3 For unproven methods, the QAPP shall provide evidence that the proposed method is capable of achieving the desired performance.

4.4 For measurements which require a calibrated system, the QAPP shall include specific calibration procedures, and the procedures for verifying both initial and continuing calibrations (including frequency and acceptance criteria, and corrective actions to be performed if acceptance criteria are not met).

SECTION 5.0, QA/QC CHECKS

5.1 At a minimum, the QAPP shall include quantitative acceptance criteria for QA objectives associated with accuracy, precision, and detection limits for critical measurements (as applicable), for each matrix.

5.2 Any additional project-specific QA objectives shall be presented in the QAPP, including acceptance criteria. This includes items such as mass balance requirements.

5.3 The specific procedures used to assess all identified QA objectives shall be fully described in the QAPP.

5.4 The QAPP shall list and define all other QC checks and/or procedures (e.g., blanks, surrogates, controls, etc.) used for the project.

5.5 For each specified QC check or procedure, required frequencies, associated acceptance criteria, and corrective actions to be performed if acceptance criteria are not met shall be included in the QAPP.

SECTION 6.0, DATA REPORTING, DATA REDUCTION, AND DATA VALIDATION

6.1 The reporting requirements (e.g., units, reporting method [e.g., wet or dry]) for each measurement and matrix shall be identified in the QAPP.

6.2 Data reduction procedures specific to the project shall be described, including calculations and equations.

6.3 The data validation procedures used to ensure the reporting of accurate project data to internal and external clients shall be described.

6.4 The expected product document that will be prepared shall be specified (e.g., journal article, final report, etc.).

SECTION 7.0, ASSESSMENTS

7.1 Whenever applicable, the QAPP shall identify all audits (i.e., both technical system audits [TSAs] and performance evaluations [PEs]) to be performed, who will perform these audits, and who will receive the audit reports.

SECTION 8.0, REFERENCES

8.1 References shall be provided in the QAPP either in the body of the text as footnotes or in a separate section.

QUALITY ASSURANCE PROJECT PLAN:

APPLICATION OF BIOREACTOR SYSTEMS TO LOW-CONCENTRATION PERCHLORATE-CONTAMINATED WATER

Bruce Logan, Ph.D.
Kappe Professor of Environmental Engineering
Penn State University

Jacimaria Batista, Ph.D.
Assistance Professor, Department of Civil
And Environmental Engineering
University of Nevada, Las Vegas

November 17, 1998

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1.0 PROJECT DESCRIPTION

1.1 GENERAL OVERVIEW

Perchlorate has recently been detected in several surface waters and groundwater wells used to supply drinking water at concentrations above the detection limit (4 ppb) to 0.37%. The California Department of Health Services (CDHS), based on EPA work, has established a provisional action level of 18 ppb for drinking water. This relatively low concentration was established because of perchlorate's interference with iodine in the production of hormones in the thyroid. The presence of perchlorate at these high concentrations in the environment, coupled with a very low drinking water standard, has created a national water contamination crisis in the US potentially affecting 12 million people. Perchlorate is readily biodegradable, and under proper conditions, can be reduced to non-detectable levels by fixed and suspended cultures of microorganisms.

Currently, there is no EPA established Maximum Contaminant Level (MCL) or Maximum Contaminant Level Goal (MCLG) for perchlorate. However, based on the guidelines established by CDHS, for the purposes of this research, the perchlorate MCLG will be considered to be <4 ppb (defined as less than the minimum detection level) and the MCL as 18 ppb.

In Phase I of the proposed research, the potential for using anaerobic, fixed-film bioreactors to treat water contaminated with perchlorate concentrations ranging from 100 to 0.1 mg/L to concentrations lower than those necessary to meet the anticipated drinking water MCL of 18 ppb will be investigated. This is a basic research project; therefore, the Quality Assurance Project Plan (QAPP) that is presented was prepared using the Category IV QAPP guidelines.

Based on the results of Phase I activities, and on engineering and economic analyses, one of the three proposed treatment systems will be recommended for further testing (Phase II). This second phase will involve on-site implementation of a specific treatment technology. It is not certain whether the reactor recommended by this project, or another project funded through the American Water Works Association Research Foundation (AWWARF), will be selected for Phase II. Therefore, since the Phase II testing of the proposed reactor system will be covered under a separate project, the presented QAPP covers only Phase I (basic research) and not field studies that will be conducted under a new grant for Phase II. Near the completion of Phase I, a separate Category III QAPP will need to be completed to discuss Phase II activities.

The research described here is a feasibility study intended to establish the most economically efficient method (from the methods shown to be technically feasible) to remove perchlorate from potential drinking water sources. Calculation of incorrect removal rates of perchlorate would result in the incorrect sizing of a reactor to be used during Phase II of research, but this QAPP is designed to avoid these errors. Specific design factors recommended during Phase I research will be tested, and refined, during subsequent Phase II work.

1.2 THE PROCESS

Bench scale experiments will be conducted on three different fixed-film biological treatment processes to determine their feasibility for being scaled up to treat large quantities of drinking water. These treatment systems are: a packed bed (slow sand filter) amended with soluble microbial carbon sources (acetate, methanol, or ethanol); a hydrogen gas fed four-phase (hydrogen gas, water, biofilm, and support media), unsaturated trickle-type packed column; a membrane-bound biofilm reactor. A detailed explanation of each reactor is included as Appendix 6.1.

Two different types of water sources will be used throughout the project. For most initial screening work, it will be necessary to control the water quality so that reactor performance can be compared (i.e. there is no variation in the water quality fed to the different reactors). Therefore, an artificial groundwater will be used in most studies conducted in Phase I. This water will be constructed using ultrapure/low ionic strength water (~0.01 mM, produced from a Millipore Academic Q water treatment system) amended with trace metals and ionic species to mimic the groundwater at the Redlands, CA, site in conductivity, major ionic species (i.e. sulfate, nitrate, phosphate), pH, and dissolved organic carbon (DOC).

Near the completion of Phase I studies, when reactor designs are optimized, a final set of experiments will be conducted using: (a) water samples from groundwater wells that have been turned off in the Redlands area (due to perchlorate contamination); (b) water from Lake Mead (spiked with perchlorate). These water samples will be used to verify the general applicability of our findings obtained using the artificial groundwater. The specific number and quantity of water samples used from Lake Mead or the Redlands area will be determined later as the research project progresses. The specific number of samples used will be a function of the number of reactor types and conditions that prove to be technically capable of perchlorate removal. There is no impact of these different water samples on the QAPP because the same reactor sampling and analytical procedures will be applied to all water samples. Informational concerning the available laboratory facilities at the two universities can be found in Appendix 6.2.

As a common starting point in our studies, we will use water containing perchlorate at 1000 ppb, with an experimental influent range of 10 to 10^5 ppb, and set as a goal a reduction to the MCLG (nondetectable, or <2.5 ppb). As indicated, there currently is no EPA established MCL or MCLG for perchlorate. Because the CDHS acceptable perchlorate level in drinking water sources is 18 ppb, biological perchlorate removal will be deemed successful if reactor effluent concentrations fall below the 18 ppb concentration. Regardless of reactor type, influent and effluent concentrations of perchlorate will be measured to determine to extent of perchlorate removal.

1.3 STATEMENT OF PROJECT OBJECTIVES

This proposal is targeted to investigate removal of perchlorate from water, leaving it suitable to be used as drinking water. The specific objectives of the proposed research grant will be to:

- Modify a sand filter to treat perchlorate-contaminated water to drinking water standards
- Design and test a gas (hydrogen) phase fixed-film bioreactor for efficiency of perchlorate removal
- Test a membrane-bound hydrogen fed biofilm reactor
- Make an economic comparison of these reactors if they were to be scaled up to capacities sufficient for treatment of large volumes of water (millions of gallons per day).

With information gained in this proposal, we will estimate the costs of treating waters using the reactors and feed substrates that successfully remove perchlorate down to drinking water levels (both <2.5 ppb and <18 ppb). Based on the engineering and economic analysis, one of these treatment systems will be recommended for further testing in Phase II at the Crafton-Redlands site in Redlands, CA.

1.4 SCHEDULE

This project will be conducted over a two-year period to begin in August of 1998. Each year is divided into three sections in order to be compatible with the preparation of reports to AWWARF every four months. In the first year, water samples from the two sites (Redlands and Nevada) would be collected and analyzed, and the three reactors built and tested using base conditions of the artificial groundwater. In the second year, the reactors would be optimized for performance by varying input loads (such as concentration of applied substrate, nutrients, etc.). The second year's work would end with an economic analysis (by CDM) and a final report submitted to AWWARF. Research at Penn State University will be conducted on the sand filter and the gas phase fixed-film bioreactor. Research at UNLV would proceed along the same time line, except that all work would be done on the membrane bioreactor. Camp, Dresser and McKee (CDM) Consulting Engineering will be responsible for working with the City of Redlands in obtaining water samples, running conventional water treatment analyses, and in the second year conducting an economic evaluation of the treatment systems' costs and projected costs for scale up of the systems. A schematic description of the research activities is included as Appendix 6.3.

During all phases of research, Frank Blaha, Project Manager, will be the point of reference at AWWARF, the organization responsible for administering funds from the East Valley Water District.

1.5 PROJECT ORGANIZATION AND RESPONSIBILITIES

This project will involve the following researchers:

- Bruce Logan, Ph.D. Kappe Professor of Environmental Engineering, Penn State University. Email: blogan@psu.edu. Telephone: 814-863-7908.
- Jacimaria Batista, Ph.D. Assistant Professor, Department of Civil and Environmental Engineering, University of Nevada, Las Vegas. 702-895-1585). Email: jaci@ce.unlv.edu. Telephone: 702-895-1585.
- Steve Price, Camp, Dresser and McKee Consulting Engineering, 100 Pringle Ave, Suite 300, Walnut Creek, CA, 94596. Email: prices@cdm.com. Telephone: 923-296-8056.

Each party's responsibilities are detailed above (Section 1.4). A list of the credentials for each PI is included as Appendix 6.4.

2.0 QUALITY ASSURANCE OBJECTIVES

2.1 EXPERIMENTAL DESIGN

The critical measurement that will be used in the evaluation of reactor performance is effluent perchlorate (ClO_4^-) concentrations. It is hypothesized that no intermediates will accumulate in solution during the reduction of ClO_4^- to chloride (Cl^-). However, potential intermediates are chlorate (ClO_3^-) and chlorite (ClO_2^-). Theoretically, concentrations of Cl^- in the treated water should be equal to the quantity of ClO_4^- removed (raw water ClO_4^- concentration - treated water ClO_4^- concentration).

Noncritical measurements will be made in an attempt to optimize reactor removal efficiency. Noncritical measurements include the reactor influent and effluent concentrations of: potential perchlorate degradation products, including ClO_3^-, ClO_2^-, and Cl^-; other potential contaminants found in water at sites in California, including TCE and PCE; energy and/or carbon sources, including acetate, methanol, ethanol (added in reactor liquid feed) and hydrogen gas (the electron donor for microorganisms in the gas phase fixed-film bioreactor); and other inorganic ions that can serve as competing electron acceptors, including nitrate (NO_3^-), and sulfate (SO_4^{2-}). Other noncritical measurements that can affect bioreactor performance, and will therefore be monitored include: pH, dissolved oxygen (DO), total organic carbon (TOC), conductivity, and oxidation-reduction potential (ORP). Table 1 summarizes the above parameters.

Table 1. Summary of critical and noncritical measurements.

Measurement	Sample Matrix	Parameter Classification
ClO_4^-	Raw water, treated water	Critical
ClO_3^-	Raw water, treated water	Noncritical
ClO_2^-	Raw water, treated water	Noncritical
Cl^-	Raw water, treated water	Noncritical
TCE	Raw water, treated water	Noncritical

PCE	Raw water, treated water	Noncritical
Acetate	Raw water, treated water	Noncritical
NO_3^-	Raw water, treated water	Noncritical
Methanol/Ethanol	Raw water, treated water	Noncritical
SO_4^{2-}	Raw water, treated water	Noncritical
pH	Raw water, treated water	Noncritical
DO	Raw water, treated water	Noncritical
TOC	Raw water, treated water	Noncritical
Conductivity	Raw water, treated water	Noncritical
Headspace hydrogen gas	Reactor headspace	Noncritical
ORP	Treated water	Noncritical

Noncritical parameters, such as NO_3^-, SO_4^{2-}, DO, and TOC will be monitored for two reasons. First, the artificial groundwater that will be used in most of our studies should be similar in quality to the actual groundwater in the Redlands area. By monitoring these parameters we can ensure that the artificial groundwater is representative of the Redlands groundwater. Second, these parameters can affect ClO_4^- removal efficiency. For instance, ClO_4^- reducing microorganisms require very low DO levels. A possible reason for lower ClO_4^- reduction could be that the DO levels in the reactor are too high. Also, NO_3^- and SO_4^{2-} may serve as alternate electron acceptors in microorganisms. Therefore, a lower ClO_4^- reduction could indicate the use of one of these terminal electron acceptors in preference to ClO_4^-. A review of ClO_3^- and ClO_4^- reducing microorganisms is included as Appendix 6.5.

Acetate, methanol, ethanol, and hydrogen gas are important noncritical parameters because they (acetate, methanol, or ethanol) serve as a carbon source and/or electron donor (hydrogen gas) to the microorganisms that will degrade ClO_4^-. If it is found that influent and effluent concentrations of a specific carbon source (e.g., acetate) are equal, then no ClO_4^- will have occurred.

A comparison of the influent and effluent concentrations of the microbial carbon source (acetate, methanol, or ethanol) will allow a determination of the proper feed quantities to enable the reactor to function most efficiently. These proper feed quantities, for the individual carbon sources, will be used in the cost analysis of reactor operation.

In the second year of study, we will introduce co-contaminants (such as TCE and PCE) at 10 mg/L levels in order to study the effect of the potential degradation of these chemicals in the highly reducing environment achieved during ClO_4^- reduction (~-300 mV; Bliven, 1996).

Reactors will be sampled for effluent ClO_4^- concentrations (single sample per detention time) until steady state conditions are achieved. Quantitatively, steady state will be defined as being achieved when effluent ClO_4^- concentrations measured over three detention times are within $\pm$ 1 standard deviation. Upon reaching steady state conditions, samples will be taken from the reactor and these samples will be those that are reported for reactor steady state conditions. A total of three reactor samples will be taken, one sample taken per detention time. Perchlorate samples (for each of three steady state detention times) will be taken in replicate, and each sample analyzed as duplicate. All other noncritical parameter

samples (for each of three steady state detention times) will be taken singularly and will be analyzed as duplicate.

The measurements (both critical and noncritical) will be made in the laboratories of Dr. Bruce Logan and Dr. Jacimaria Batista at The Pennsylvania State University (University Park, Pennsylvania) and The University of Nevada, Las Vegas (Las Vegas, Nevada), respectively.

2.2 DETERMINING QA OBJECTIVES

The purpose of establishing QA objectives for this research is to ensure that the data generated throughout the project are of acceptable quality so that the project's technical objectives are achieved.

2.3 QUANTITATIVE QA OBJECTIVES: ACCURACY, PRECISION, METHOD DETECTION LIMIT, AND COMPLETENESS

Accuracy. The accuracy of effluent ClO_4^- concentration measurements will be determined based on calibration techniques outlined by the equipment manufacturer. The validity of the constructed calibration curves will be determined by performing a linear least squares analysis. Water samples received (Section 1.1.1) will be spiked with a known concentration of ClO_4^- to determine the accuracy of laboratory techniques.

Accuracy of in-house ClO_4^- measurements will also be determined monthly by analyzing blind samples that have been prepared by Dr. Jaci Batista (if determining accuracy of laboratory procedures conducted at Penn State), or prepared by Dr. Bruce Logan (if determining accuracy of laboratory procedures conducted at UNLV).

Precision Samples used for ClO_4^- concentration determination will be reported as the average of duplicate analyses of each replicate sample. Precision of these multiple analyses will be measured by calculation of the relative percent deviation (RPD).

Minimum detection level The MDL for ClO_4^- method will be computed by injecting 7 samples of 5 ppb into the IC unit and computing the peak area given by the 7 injections. The standard deviation of the 7 corresponding peak areas will be calculated and subsequently, the MDL will be calculated as:

$$MDL = (SD * t * C)/Am$$

where:
- SD = the standard deviation of the 7 areas recorded
- t = student distribution for n=7
- C = 5 ppb
- Am = the mean area of the 7 peak areas measured

The above method for determining the ClO_4^- method follows Standard Method 1030-E (Standard Methods 19th edition, 1995).

Dionex defines the MDL of its instruments as 2.5 ppb; however, researchers have been able to obtain lower concentrations (Batista, 1998). Therefore, an in-house MDL will be determined, and as long as it $\leq$ 2.5 ppb, it will be accepted as the MDL.

Completeness Completeness is a measurement of the amount of valid data obtained compared to the total amount of data collected. The degree of completeness is the number of samples with acceptable data divided by the total number of samples collected and tested, and multiplied by 100.

Table 2 summarizes the quantitative QA objectives for the critical parameter ClO_4^- concentration. Perchlorate concentrations will be measured in the untreated reactor influent water and treated reactor effluent water.

Table 2. Summary of QA objectives for the critical parameter (ClO_4^-).

Critical Measurement	Matrix	Method	Reporting Units	MDL[a]	Precision[b] (RPD)	Accuracy[c] (% Recovery)	Completeness[d]
Perchlorate	Untreated raw water	Ion Chroma-tography	ppb	$\leq$2.5	$\leq$ 20	80-120	95
Perchlorate	Treated water	Ion Chroma-tography	ppb	$\leq$2.5	$\leq$ 20	80-120	95

(a) Minimum detection level
(b) Given as RPD for laboratory replicate samples
(c) As percent recovery of matrix spike
(d) Based on the number of valid measurements, compared to the total number of measurements

Average effluent ClO_4^- concentrations will have to satisfy the QA objectives outlined in Table 2. If the QA objectives are not met, adjustments will be made to the experimental conditions and measurements will be conducted again.

2.4 QUALITATIVE QA OBJECTIVES: COMPARABILITY AND REPRESENTATIVENESS

Comparability Comparability is a qualitative parameter that expresses the degree of confidence that data are equivalent for a specific parameter or group of parameters. Comparability of the data obtained here to other data sets will be achieved by strict observance of typical analytical procedures (Section 3.3). Accurate and prompt tabulation of data will also aid comparability.

Representativeness. The degree to which sample data accurately and precisely represent the characteristics of a population, parameter variation at a sampling point, or an environmental condition is defined here as sample representativeness. Consistent sampling procedures and frequent sampling throughout the operation of the reactor will achieve representativeness and comparability.

2.5 OTHER QA OBJECTIVES

No further QA objectives are expected.

2.6 WHAT IF QA OBJECTIVES ARE NOT MET?

A lack of precision and accuracy will be corrected by employing corrective actions. Examples of possible corrective actions include reanalyzing samples, checking equipment for possible malfunctioning, checking mathematical calculations, or modifying sampling method/bioreactor design.

Data will be promptly evaluated to determine whether individual QA objectives are being achieved so corrective action can be immediately taken if necessary (corrective action will be noted in log book).

If particular QA objectives are not met, data will be noted and a discussion will made in each progress report, as well as in the final report, relating the significance of the particular QA objectives not being achieved.

3.0 SAMPLING AND ANALYTICAL PROCEDURES

3.1 SAMPLING PROCEDURES

The exact design of the individual reactors (Section 1.1.1) has not yet been determined as their design is a goal of this research. Therefore, exact sampling locations cannot yet be specified, but at a minimum, reactor influent and effluent conditions will be monitored. It is anticipated that 2-3 other sampling ports will also be located throughout the column depths (applies to modified sand reactor and gas-phase fixed-film reactor). Influent feed and effluent ports will most likely be the only sampling locations on the membrane bound reactor. When reactor design is finalized, sampling procedures will be developed to allow a representative and contaminant free sample to be obtained.

Table 3 summarizes all analysis parameters (both critical and noncritical) that will be measured, and the liquid volumes that will be necessary for each analytical procedure.

Table 3. Summary of sample parameters.

Analysis Parameter	Container Size	Sample Quantity Required for Analysis
Conductivity	20 mL	5 mL
ORP	20 mL	5 mL
Hydrogen gas	100 uL syringe	100 uL syringe
Cl^-	20 mL	5 mL[a]
pH	20 mL	5 mL
NO_3^-	20 mL	5mL[a]
DO	20 mL	5 mL
TOC	20 mL	3 mL
ClO_4^-	20 mL	5mL[a]

ClO_3^-	20 mL	5mL[a]
ClO_2^-	20 mL	5mL[a]
Acetate	20 mL	5mL[a]
NO_3^-	20 mL	5mL[a]
Methanol/Ethanol	20 mL	5 mL
SO_4^{2-}	20 mL	5mL[a]
TCE	20 mL	1 mL
PCE	20 mL	1 mL

(a) all parameters that will be determined by ion chromatography require 5 mL volume, which can be analyzed once, or as a duplicate or a triplicate. Actual sample volume may be less than 5 mL, when sample requires dilution to bring expected concentration into range of ion chromatography machine detection.

Reactor effluent samples will be collected in glass or HDPE containers, while TCE and PCE samples will be collected in crimp-sealed vials (to allow for zero headspace in sample bottle). If the sample to be collected is to be used in the determination of TOC or DOC, a glass sample container that has been previously fired in a muffle furnace (to remove residual organic material) will be used. HDPE sample containers will undergo triplicate rinses in MilliQ water (Section 1.2) and will be reused.

Samples will be analyzed as soon as possible after collection, but holding times will be less than seven days. Samples that are not analyzed immediately will be stored on ice.

All water samples from non-laboratory sites (water from Lake Mead or groundwater from Redlands, CA) will be shipped in 55-gallon drums and stored in a refrigerator at 4°C. The drums will be constructed of plasticizer-free plastic, and a comparison of water sample DOC will be made before and after sample shipment.

Smaller samples will be shipped using overnight mail, and preserved with dry ice to keep them cool during shipping. Water samples will be held in polycarbonate carboys (made of plasticizer-free plastic). Perchlorate is non-volatile and non-adsorbing, and therefore we do not expect any degradation of samples during shipping. Soil samples used to develop a ClO_4^- degrading consortium will be placed in 5 gallon carboys. Cooling these samples is essential to preserve the microbial community in the samples. Samples will be marked to indicate: person taking samples, date, time, contents (water), location sample obtained, conditions (temperature), and date received.

Details of sampling procedures and results of all analyses will be kept in hand-written, bound laboratory notebooks that will be available for inspection. All analytical results will be calculated using appropriate equations and reported in appropriate concentration units (mg/L or ppb). Reduced data will be transferred to spreadsheets, and will be periodically reviewed by the analyst and principal investigator. All data classified as outliers (data that does not satisfy QA objectives) will be immediately examined in detail and corrective actions taken.

3.2 PROCESS MEASUREMENTS

Field process measurements are not a component of the Phase I research project.

3.3 ANALYTICAL PROCEDURES AND CALIBRATION

Water samples from the Redlands and Nevada sites will be analyzed for Cl^-, TCE, PCE, NO_3^-, SO_4^{2-}, pH, and conductivity by an EPA certified commercial water laboratory.

Sands used in columns will be analyzed for size distribution and organic carbon. Sand grain sizes will be measured by sieving, followed by image analysis of particle sizes (Galai Image analysis system) to determine the particle size distribution within size classes. Organic carbon will be measured through combustion by a commercial laboratory.

Perchlorate concentrations above 1 mg/L can be analyzed using an ion specific probe (Orion Research Inc.), and verified by ion chromatography (Dionex DX-100, DX-500 at Penn State; DX-120 at UNLV). The perchlorate specific probe will only be used as a monitoring tool to gauge the performance of a reactor (i.e. prior to steady state reactor operation). All final data that will be reported on steady state reactor performance will be measured using an IC. For verification of perchlorate probe measurements at >1mg/L concentrations, and analysis of samples at concentrations of 2.5 ppb (detection limit) to 1 mg/L or 20 mg/L (see below), we will use the perchlorate IC method developed by Dionex. The Dionex method is included as Appendix 6.6.

3.3.1 EPA-Approved or Other Validated Standard Methods

Sample concentrations of the following noncritical measurements will be conducted according to Standard Methods for the Examination of Water and Wastewater (1995): Cl^-, acetate, TCE/PCE, conductivity, ORP, reactor headspace hydrogen gas ($H_{2(gas)}$), pH, DO, TOC, NO_3^-, and SO_4^{2-}. Methanol/ethanol aqueous concentrations, ClO_2^-, and ClO_3^- concentrations (noncritical measurements) will be measured according to USEPA Methods.

TOC measurements for all water samples will be determined by a Shimadzu TOC 5000A, which uses a platinum catalyst combustion method. Prepared standards will be spiked with ethanol or methanol to determine if the analytical method is sensitive to these noncritical analytes. It will be assumed that any volatile organic compound (e.g. TCE, PCE) will be sparged by the nitrogen flow, and therefore will not be included in the TOC measurement.

Sample ClO_4^- concentrations (critical measurement) will be measured according to the Dionex method (Appendix 6.6). The Dionex method is the same as the CA Department of Health Method, except different eluents are used (sodium hydroxide in Dionex method, para-cyanophenoxide in CA Dept Health method). Prior to its use in the IC unit, the sodium hydroxide eluent will be vacuumed to de-gas the solution. A 1-L solution of sodium hydroxide can be used for up to a month (Dionex, 1998), but will likely be used much more rapidly. Perchlorate can be measured down to concentrations of 4 ppb using a Dionex DX-500 with an AS-11 column, with a 100 mM NaOH solution, sparged with helium gas, as eluent (Wirt et al. 1998). For concentrations up to 1000 ppb, a 1 mL injection is used; at higher concentrations, a 25 uL injection is used. Concentrations larger than 20 mg/L are diluted manually with ultrapure water.

Chloride and acetate (noncritical measurements) are similarly measured on the IC, except the necessary eluent is 0.3 mM $NaHCO_3$+0.9 mM Na_2CO_3 and only the 25 uL injection loop is used. An AS-4 column will be used in the determination of Cl^- and acetate by IC.

In all IC measurements, the liquid sample will be filtered using 0.25 um polycarbonate filters before injection into the IC.

Table 4 summarizes these analytical methods.

Table 4. Method description of analytical techniques.

Parameter	Method Number	Method Title	Source(Reference)
ClO_4^-		Analysis of Low Concentrations of Perchlorate in Drinking Water and Ground Water by Ion Chromatography	Dionex
Methanol/ Ethanol	USEPA Method 8015		USEPA (2)
ClO_3^-	USEPA Method 300.1		USEPA (2)
ClO_2^-	USEPA Method 300.1		USEPA (2)
Cl^-	4500-Cl^- F	Chloride-Ion Chromatography Method	Standard Methods (1)
Acetate	4110	Determination of Anions By Ion Chromatography	Standard Methods (1)
TCE/PCE	6232 B.	Liquid-Liquid Extraction Gas Chromatographic Method	Standard Methods (1)
Conductivity	2510 B.	Conductivity-Laboratory Method	Standard Methods (1)
ORP	2580 B.	Oxidation-Reduction Potential Measurement in Clean Water	Standard Methods (1)
$H_{2(gas)}$	2720 C.	Anaerobic Sludge Digester Gas Analysis-Gas Chromatographic Method	Standard Methods (1)
pH	4500-H^+	pH Value-Electrometric Method	Standard Methods (1)
DO	4500-O	Oxygen (Dissolved)-Membrane Electrode Method	Standard Methods (1)
TOC	5310 B.	Total Organic Carbon (TOC)-Combustion-Infrared Method	Standard Methods (1)
NO_3^-	4500-NO_3^--C	Nitrogen (Nitrate)-Ion Chromatographic Method	Standard Methods (1)
SO_4^{2-}	4500-SO_4^{2-}B	Sulfate-Ion Chromatographic Method	Standard Methods (1)

(1) Standard Methods for the Examination of Water and Wastewater (1995)
(2) Methods for Chemical Analysis of Water and Wastes (1979)

3.3.2 Nonstandard or Modified Methods

Perchlorate will be measured at concentrations above 1 mg/L using a ClO_4^- specific probe (Orion Research Inc.). Interferences by other anions are known, and include for example at the 10 mg/L concentration: I^-, 25 mg/L; ClO_3^-, 166 mg/L; NO_3^-, 310 mg/L; SO_4^{-2}, 19,200 mg/L. In order to assure that other anions do not interfere with the values obtained using the ClO_4^- probe, we will verify probe results using the Dionex IC method for any new water

sample received (i.e. water from Lake Mead or groundwater from Redlands, CA). It should be emphasized that the ClO_4^- probe will only be used for determining ClO_4^- concentrations before a reactor reaches steady state. All ClO_4^- data that will appear in quarterly and the final report will be measured using the Dionex method.

3.3.3 Calibration Procedure and Frequency

Our ion chromatograph (IC) has an autosampler. The following calibration procedure will be used before each day's sample analysis. Each step represents a run through the IC unit.

1. Deionized water sample
2. Deionized water sample
3. Calibration standard-Level 1- 5 ppb ClO_4^-
4. Calibration standard-Level 2- 10 ppb ClO_4^-
5. Calibration standard-Level 3- 15 ppb ClO_4^-
6. Calibration standard-Level 4- 30 ppb ClO_4^-
7. Calibration standard-Level 5- 60 ppb ClO_4^-
8. Calibration standard-Level 6- 80 ppb ClO_4^-
9. Calibration standard-Level 7- 100 ppb ClO_4^-
10. Deionized water sample
11. Deionized water sample

After the calibration procedure is complete and a R^2 value (from linear least squares analysis) of 0.997 or greater is achieved, the following sampling procedure will be used.

1. Run samples
2. Run Quality Control (QC) and mid-standard check

This procedure will be repeated provided that the QC and mid-standard check have accurate results. A QC sample is a sample prepared by a member of the research group, different from the person who prepared the calibration standards. A mid-standard check consists of injecting one of the standards after every 20 samples, to check the accuracy of the calibration.

If the R^2 value of the ClO_4^- standard curve is not ≥ 0.997, the calibration standards will be reanalyzed, and a new calibration curve constructed. If the criterion of $R^2 \geq 0.997$ is again not met, new standards will be prepared and the process repeated. The IC will also be examined to make sure that it is functioning properly.

The ClO_4^- ion specific probe will be calibrated daily using four calibration standards at concentrations of 5, 10, 25, and 50 mg/L. If it is expected that the sample concentration will be above 50 mg/L, the sample will be diluted.

Calibration of other analytical equipment used for the determination of noncritical parameters will follow procedures described by equipment manufacturer. For example, DO probe will be air calibrated, pH meter will be calibrated against two known pH solutions,

etc. Calibration standards will be prepared using the same methods as used to prepare the samples in order to reduce bias from the preparation method. Reagents used in the preparation of all standard solutions will be ≥99% pure.

The validity of the constructed calibration curves will be determined by performing a linear least squares analysis.

4.0 APPROACH TO QA/QC

4.1 INTERNAL QUALITY CONTROL

As stated previously, ClO_4^- calibration standards and spiked water samples (from Lake Mead and groundwater from Redlands, CA) will be prepared using ≥99% pure standards, and the standards will be prepared using Milli-Q water (18 MΩ cm DI water). A 7 point calibration curve will be generated on the IC (4 point for ClO_4^- probe). Acceptable goodness of fit will require a R^2 ≥0.997 (for IC method; 0.97 for probe method). Duplicate sample analyses will agree in precision to ± 20% RPD. Each new water sample received (from Lake Mead or Redlands, CA), will be spiked with ClO_4^-, and will have a percent recovery of ± 20%. Prepared blind samples that are tested monthly (Section 2.3) will have a percent recovery of ± 20% as well. A QC sample and mid-standard check (Section 3.3.3) will also be run with each set of samples on IC check the accuracy of the calibration procedure.

4.2 CALCULATION OF DATA QUALITY INDICATORS

4.2.1 Precision

The calculation of relative percent difference (RPD) for duplicate measurements will be calculated as outlined in Category IV Prep Aids (Simes, 1991).

4.2.2 Accuracy

The calculation of matrix spike percent recovery will be calculated as outlined in Category IV Prep Aids (Simes, 1991).

4.2.3 Completeness

Completeness will be calculated as outlined in Category IV Prep Aids (Simes, 1991).

4.2.4 Method Detection Limit (MDL)

The MDL for the determination of ClO_4^- concentrations will be calculated as per Standard Method 1030-E (Standard Methods, 19th edition).

5.0 REFERENCES

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A list of references that are referred to in Appendices 6.1-6.6 is given as Appendix 6.7.

6.0 APPENDICES

Appendix 6.1 REACTOR TYPES AND CONFIGURATION

Given that large volumes of non-sterile water will pass through the reactor, it will be impossible to maintain pure culture conditions in the bioreactors; therefore, the reactors must be designed to operate using mixed cultures. While it may not necessary to operate the reactor as a pure culture, it still may be helpful to inoculate it with either an adapted culture or a known strain of cells in order to rapidly develop a perchlorate respiring population in the reactor. Such an acclimated mixed culture is easily obtained via standard enrichment techniques using wastewater or soil samples (Bliven 1996, Olsen 1997, Logan et al. 1998). For reasons of public acceptability, we would obtain an enrichment culture from the Nevada Wash in Las Vegas (where soils have long been exposed to perchlorate), or use isolates from such a culture. We have already obtained soil samples from this area and are in the process of characterizing these bacteria. (Funding for current work on obtaining and studying (per)chlorate reducing isolates is from in-house funds and a grant from NSF on chlorate respiring microorganisms). These microbial strains and communities would be used in reactors described below. It should also be noted that in hydrogen gas reactors, it may also be desirable to bioaugment the system with a strain of microbe capable of dehalogenating chlorinated aliphatic molecules (see below, section 4.4.7). In all cases, however, it is recognized that the reactors will need to operate as mixed cultures. Strategies to maintain a dominant perchlorate respiring culture, such as media mixing and culture regeneration, will be examined as described below.

6.1.1 Sand Column Fixed-Film Bioreactor

This perchlorate biofilm reactor will be an anaerobic biofilm packed bed reactor used specifically to grow perchlorate-respiring bacteria and treat water (surface water and ground water) to remove perchlorate to the ppb range or lower. The reactor will consist of a laboratory-scale sand column of the type typically used for water treatment following coagulation/ sedimentation tanks, but modified to allow for the introduction of chemical substrates to serve as an electron donor (Figure 1). The filter will be a dual media filter operated in either up-flow or down-flow mode, with most of the filter composed of sand with the bottom media consisting of gravel. The reactor would be inoculated, and operated in recycle mode until a biofilm had been developed as indicated by a loss of perchlorate in the system. The system would be fluidized (i.e. backwashed), but it would be done very gently and for the sole purpose of homogenizing the column media. The reactor could then be operated again in plug flow mode again with fresh feed water containing one of the supplemental carbon sources and perchlorate-amended artificial groundwater.

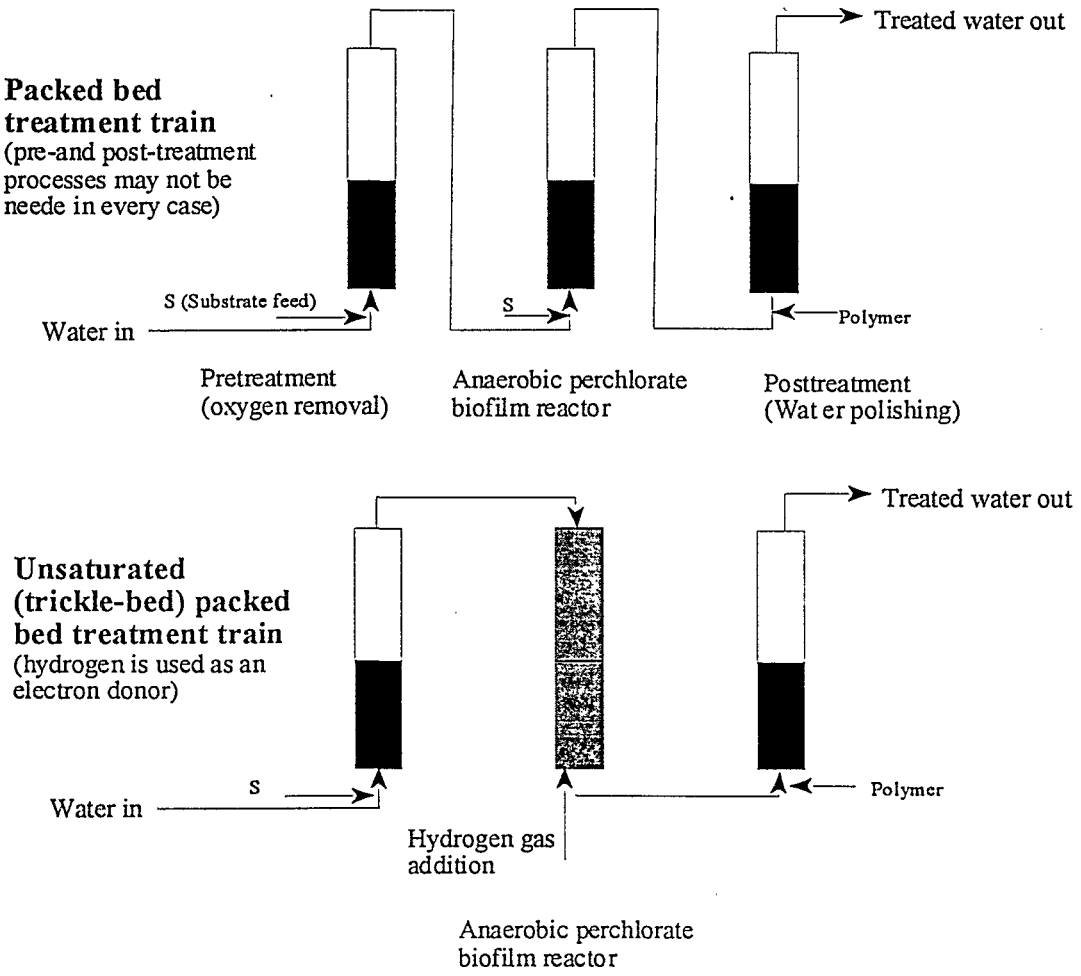

Figure 1. (A) Process train for treating perchlorate contaminated water. The pre-and post-treatment trains may not be needed in all cases. Pretreatment functions to consume all oxygen for the anaerobic perchlorate biofilm reactor, while posttreatment is provided to remove any sloughed biofilm and to provide for biological polishing of any remaining growth substrate (S) in the water sample. (B) Here, the biofilm reactor is shown to contain a gas phase of hydrogen that serves as the electron donor in the biological process.

There are two important components to this reactor: the ability to regenerate the biofilm; and the ability to fluidize and mix the filter media. Because of the low perchlorate concentrations present in many drinking water sources, there might not be sufficient perchlorate in the water to support a perchlorate respiring biofilm in competition with other anaerobes (such as methanogens) even though the cell yields and growth rates of these other anaerobic communities are so low compared to perchlorate respiring strains. Thus, we anticipate needing to periodically regenerate a thick perchlorate respiring biofilm by periodically infusing the column with high concentrations of chlorate (not perchlorate) and substrate. The biofilm in this reactor would therefore be regenerated by: temporarily halting the flow of contaminated water through the reactor; recycling water containing relatively high concentrations of electron donor and electron acceptor (chlorate, at 10-1000mg/L levels) to that bacteria so that they may into a thick biofilm; the reactor would then be rinsed

with clean water, and placed back into service. Thus, the bacteria in the biofilm would scavenge perchlorate while in endogenous decay. The biofilm would be regenerated as often as necessary, but it should certainly be on a less frequent time scale than needed for a water treatment filter for ordinary backwashing.

Second, the reactor will be able to be periodically fluidized for two reasons. One, it may be necessary to periodically redistribute bacteria that preferentially will grow near the column effluent to the whole column. Two, it may be necessary to periodically dislodge old biofilms (or other material that may accumulate on the media packing) to prevent the sand bed from clogging. The need to only periodically fluidize the bed, versus continuously fluidize the bed (as proposed by others) means that operation costs are substantially reduced for normal operation compared to a fluidized bed.

Contaminated water from the regeneration cycle (possibly containing high concentrations of chlorate or electron donor) would be held for subsequent treatment. Excess chlorate would rapidly be removed in the presence of excess electron donor. Excess electron acceptor could be removed through ordinary anaerobic treatment processes such as methanogens. In our laboratory, we find that water in batch culture can be disposed of after a day or so. In a water treatment plant, we expect such water could be added back into the flow entering the perchlorate reactor.

As described above, perchlorate removal from 20 mg/L to 18 μg/L in sand columns has already been proven in our laboratory (Logan and Kim 1998) at loading rates of <0.11 gpm/ft^2. Higher loading rates (>0.12 gpm/ft^2) resulted in perchlorate breakthrough producing high effluent concentrations (>150 μg/L) that rapidly increased with hydraulic loading. However, substrate (acetate) concentrations would need to be optimized in order to minimize effluent substrate concentrations. These loading rates are also quite low (relative to water treatment filters). It is hoped that operation strategies related to biomass redistribution and regeneration will allow these loading rates to be increased making the process more economically efficient.

6.1.2 Hydrogen-fed Gas Phase Unsaturated Fixed-Film Perchlorate Reactor

It is undesirable to operate a water treatment reactor under conditions that leave high concentrations of oxidizable substrate in the water as this could lead to increased bacterial growth in water distribution lines. In order to avoid any problems with excess substrate (such as methanol, ethanol or acetate) remaining in the reactor, we propose to design an unsaturated media filter using hydrogen as an electron donor. CRMs have been found to be able to use hydrogen (van Ginkel et al. 1995) and to fix carbon using carbon dioxide. Because PRMs are also CRMs, we believe it should be possible to remove perchlorate using hydrogen as a feed. Hydrogen is sparingly soluble, and thus would not accumulate in water leaving the plant, it is non-toxic, and can easily be generated on any site electrolytically using only water. While the hydrogen would be consumed by the microorganisms, oxygen could either be captured and re-sold, or used as an oxygen source for post-treatment polishing of the effluent in a downstream reactor.

The hydrogen reactor consists of packing (likely plastic support media) to provide a high surface area to volume ratio, and also a high void fraction to avoid clogging and therefore for this case, not to necessitate backwashing (Figure 1). Hydrogen gas (either fed from a containerized source or created on site electrolytically or by another means) would be added into the reactor gas phase, but oxygen would be excluded from the gas phase. Oxygen can easily be consumed with a platinum catalyst in the gas phase, although this would only need to be used during start up or during times when the reactor is exposed to air (or turned off for long periods of time). We assume that any oxygen in the water entering the reactor would be quickly consumed by the biofilm. The water would trickle down through the reactor, so that the microbes growing on the column packing could use the hydrogen gas as an electron donor (food source) and use the perchlorate as an electron acceptor (for respiration) accomplishing perchlorate removal. Thus, this reactor is essentially a type of trickling filter reactor commonly used for wastewater treatment and gas transport into the wetted film can be described by adapting gas transport models for fixed film systems (Logan et al. 1993)

The design of such gas phase reactors for water treatment has been tried in the past. For example, it has been proposed to treat waters contaminated with volatile organic compounds, such as TCE, using methanotrophs (methane oxidizing bacteria). We would use the results of those studies in considering additional details of our reactor design. The main limitations of these methanotrophic reactors, versus those proposed here, is that toxic intermediates are produced during TCE breakdown but such toxic intermediates do not accumulate during perchlorate degradation.

6.1.3 Membrane-Biofilm Reactor

A disadvantage of the above systems is that bacteria used to degrade the perchlorate will come directly into contact with the water being treated. It is possible to design a biological reactor using a semi-permeable membrane so that the bioreactor is kept separate from the water sample (Sakakibara et al. 1994, Metcleaf and Schroeder 1995). Therefore, it is proposed to build and test a combined reactor consisting of a diffusion reactor (DR) and a biological reactor (BR), separated by a microporous membrane (Figure 2). (This part of the research project would be conducted as a subcontract to Dr. Jaci Batista at UNLV). In this membrane-bioreactor setup, a perchlorate contaminated stream is allowed to flow into the DR chamber, and a concentration gradient is set up across the microporous membrane by consumption of perchlorate in the BR chamber. Chloride can diffuse back into the DR chamber preventing the buildup of ions in the BR chamber.

There is no need to maintain a pressure difference across the membrane because the transport of ions is solely based on diffusion, and therefore the resulting process is not energy-intensive. The pore size of the microporous membrane will be chosen so that perchlorate can diffuse into the BR chamber while the back transport of microbial cells and macromolecules into the DR chamber is minimized. A hydrogen oxidizing biofilm will be developed to reduce perchlorate. Because hydrogen is maintained on one side of the biofilm, and the perchlorate diffuses from the other side, the loss of hydrogen can be

minimized by adjusting the hydrogen atmosphere in the BR chamber in order to meet the perchlorate flux across the membrane.

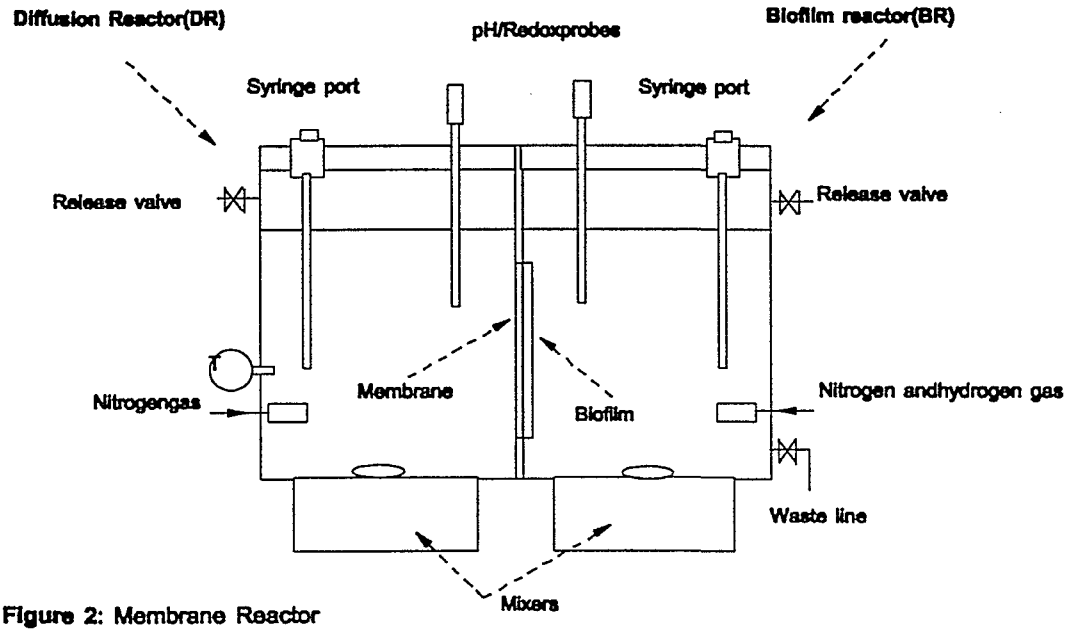

Figure 2: Membrane Reactor

Mass transport and microbial kinetics can be separately determined. The diffusion rate across the membranes will be computed by filling both tanks with perchlorate-free water and then spiking the DR tank with the perchlorate and measuring contaminant concentration in both chambers as a function of time. A range of perchlorate concentrations from 0.1 to 100 mg/L will be tested. Initially, samples of the BR tank every 15 minutes but this is subject to changes based on initial perchlorate concentration in the DR tank. Microbial kinetics will be calculated as indicated above for other biofilm reactors.

Appendix 6.2 DESCRIPTION OF FACILITIES

This research project will be conducted at primarily at Penn State, under the direction of Dr. Bruce Logan. Laboratory studies, as described in the previous section, for the sand and hydrogen gas reactor would be performed in the Kappe Laboratories (see facilities below). The co-PI at UNLV, Dr. Jaci Batista, will direct research related to the membrane-biofilm reactor. Facilities available in her laboratory are also described below.

Facilities available at Penn State. The Kappe Laboratories are located in the Sackett Building on the main campus, and in the Wastewater Treatment Laboratories, and cover an area of approximately 14,000 ft^2. The laboratories are supervised by a full time Laboratory Manager (Mr. Gerry Zimmerman). Major equipment in the Kappe Environmental Engineering laboratories include:

- Ion chromatographs (2): Dionex dx-500 and DX-100, both with autosamplers for detection of chlorate, perchlorate, and other anions;
- Gas chromatographs (4): Varian models 3400 (2); Hewlett Packard model 5870 GC; SRI 8610.
- Carbon analyzers with autosamplers (2): Shimadzu TOC 5000A; Dohrmann TOC analyzer.
- Particle counters (3): Coulter Counter Multisizer 2 (resistance-type) with computer interface; Coulter PCA 2; Galai CIS-100 laser particle counter with computer interface system.
- High- pressure liquid chromatographs (2): Hewlett Packard 1100 LC and a Waters M-501.
- UV spectrophotometers (2): Shimadzu UV 1601 and Perkin Elmer.
- Atomic absorption spectrophotometer (Perkin-Elmer Model 3030B).
- Anaerobic chamber: Coy 7080 with heated chamber and oxygen:nitrogen detector.
- Micrometrics 2000 Accelerated Surface Area and Porosimetry Units (2) with Density functional theory pore analysis software; Thermogravimetric analyzers (2): Cahn TG-131, TG-121; Accelerating rate calorimeter (CSI); Thermal reactivation furnace (Applied Test Systems 3210).
- Microscopes: Zeiss Axiophot microscope with image analysis and photometric detection; Olympus BH-2 with image analysis and epifluorescence capabilities.
- Various other equipment including: Microbics Toxicity Analyzers (2): Model 2055, Model 500; Walk-in environmental chambers (4); Anaerobic and aerobic respirometer systems; Laminar flow hood for sterile microbiological work: Biosafety Class II; vertical flow; Fisher Scientific; Fermentors (2) capable of operating in batch or chemostat mode: Centrifuges (3): Sorvall 5C high speed refrigerated; benchtop refrigerated centrifuge (Eppendorf 5403) with various rotors for medium to small sample volume; microcentrifuge (Eppendorf 5415) for small (1.5 ml) samples; Ozone Analyzer (Dasibi Environmental Corp 1008-HC); UV lamp advanced oxidant generation system; Membrane filtration systems (2): Reverse osmosis unit (Desal); ceramic cross flow membrane apparatus (MSC Liquid Filtration Corp.); various ovens; laboratory shakers, filtration boxes, ultrafiltration cells, rotoevaporator (Buchi Rotavapor, R-114); Millipore Academic-Q ultrapure water system with RO pretreatment; and balances.

Facilities at UNLV. The co-PIs research laboratory at the University of Nevada Las Vegas (UNLV) occupies 1,200 sq ft. The facilities includes: an Ion-chromatograph (Dionex-DX 100 with conductivity and electrochemical detectors) for measuring perchlorate, fume hoods, electronic balances, pH meters, ovens, optical microscope, glassware and major analytical equipment such as an atomic adsorption spectrometer (Perkin-Elmer 4100 Zeeman), gas chromatographs (Hewlett Packard 5890 series), total organic carbon analyzer (ASTRO 2001), UV-visible spectrophotometer, desktop spectrophotometer, autoclave, IBM-PC for data collection, Hach COD digestor, turbidity meter, conductivity meter, dissolved oxygen meter, and a jar test device for flocculation studies.

Appendix 6.3 PROJECT SCHEDULE ACCORDING TO RESEARCH TASK AND YEAR.

Year	Research Tasks by PI/Location	
	PI: Bruce Logan/Penn State	co-PI: Jaci Batista
Year 1 (1998-1999)	Build reactors, develop perchlorate degrading consortium. Obtain water samples and characterize water.	Same tasks as outlined for PSU work, except all tests done using membrane reactor.
	Perform first set of laboratory experiments (sand and hydrogen-gas reactors) to identify reactor performance under base conditions.	
	Test different feed substrates for perchlorate removal efficiency.	
Year 2 (1999-2000)	Vary inlet concentrations of perchlorate, applied substrate concentrations.	
	Optimize reactor conditions and perform economic comparisons of design.	
	Write up final report on reactor performance and comparisons.	

Appendix 6.4 CREDENTIALS OF INVESTIGATORS

BRUCE ERNEST LOGAN

Kappe Professor of Environmental Engineering, Dept. Of Civil and Environmental Engineering,
The Pennsylvania State University, University Park, PA 16802-1479
Phone: 814-863-7908, Fax: 814-863-7304, Email: blogan@psu.edu

EDUCATION

1986 Ph.D. in Environmental Engineering, University of California, Berkeley
1980 M.S. in Environmental Engineering, Rensselaer Polytechnic Institute
1979 B.S. in Chemical Engineering, Rensselaer Polytechnic Institute

EXPERIENCE

1997 - present Kappe Professor, Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA.

1986 - 1997 Associate Professor (1992-1997), Assistant Professor (1986-1992), Dept. of Chemical and Environmental Engineering; Investigator, Center for Toxicology (1993-1997), University of Arizona, Tucson, AZ.

1980 - 1982 Hazardous Waste Specialist and Waste Treatment Engineer, Stone and Webster Engineering Corporation, Boston, MA.

JOURNAL PUBLICATIONS- most related to Proposed Project (partial list)

Logan, B.E., A.R. Bliven, S.R. Olsen, and R. Patnaik. 1998. Growth Kinetics of Mixed Cultures under Chlorate-Reducing Conditions. *J. Env. Engrg.*, In press.

Logan, B.E. 1998. A review of chlorate and perchlorate respiring microorganisms. Bioremediation J. Submitted.

Camesano, T.A. and B.E. Logan. 1998. Influence of fluid velocity and cell concentration on the transport of motile and non-motile bacteria in porous media. *Environ. Sci. Technol.*, In press.

Martin, M.J., B.E. Logan, W.P. Johnson, D.J. Jewett, and R.G. Arnold. 1996. Scaling bacterial filtration rates in different sized porous media. *J. Environ. Engng.*, 122(5):407-415.

Aiken, B.S. and B.E. Logan. 1996. Degradation of pentachlorophenol by the white rot fungus *Phanerochaete chrysosporium* grown in ammonium lignosulphonate media. *Biodegradation,* 7(3):175-182.

Alleman, B.C., B.E. Logan, G.L. Amy and R.L. Gilbertson. 1995. Degradation of pentachlorophenol by white rot fungi in rotating tube bioreactors. *Wat. Res.* 29(1):61-67.

Logan, B.E. 1993. Oxygen transfer in trickling filters. *J. Environ. Engin.* 119(6):1059-1076.

Logan, B.E., S.W. Hermanowicz and D.S. Parker. 1987. A fundamental model for trickling filter process design. *J. Water Pollut. Control Fed.*, 59(12):1029-1042.

JOURNAL PUBLICATIONS- OTHER

Logan, B.E. 1998. Environmental Transport Processes. Wiley, New York. (Accepted for publication)

Confer, D.R., and B.E. Logan. 1998. Location of protein and polysaccharide hydrolytic activity in suspended and biofilm wastewater cultures. *Wat. Res.*, 32(1):31-38.

Confer, D.R. and B.E. Logan. 1997. Molecular Weight Distribution of Hydrolysis Products during Biodegradation of Model Macromolecules in Suspended and Biofilm Cultures II: Dextran and Dextrin. *Wat. Res.*, 31(9):2137-2145.

Logan, B.E. and R. Patnaik. 1997. A gas chromatographic based headspace biochemical oxygen demand test. *Water Env. Res.*, 69(2):206-214.

Li, X. and B.E. Logan. 1997. Collision Frequencies of Fractal Aggregates with Small Particles by Differential Sedimentation. *Environ. Sci. Technol.*, 31(4):1229-1236.

Logan, B.E., D.G. Jewett, R.G. Arnold, E. Bouwer and C.R. O'Melia. 1995. Clarification of clean-bed filtration models. *J. Environ. Eng.* 121(12): 869-873.

Gross, M.J. and B.E. Logan. 1995. Influence of different chemical treatments on transport of *Alcaligenes paradoxus* in porous media. *Appl. Environ. Microbiol.*, 61(5):1750-1756.

Logan, B.E. and J.R. Kilps. 1995. Fractal dimensions of aggregates formed in different fluid mechanical environments. *Water Res.* 29(2):443-453.

Haldane, G.M., and B.E. Logan. 1994. Molecular size distributions of a macromolecular polysaccharide (dextran) during its biodegradation in batch and continuous cultures. *Wat. Res.* 28(9):1873-1878.

Logan, B.E., B.C. Alleman, G.L. Amy and R.L. Gilbertson 1994. Adsorption and removal of pentachlorophenol by white rot fungi in batch cultures. *Wat. Res.* 28(7):1533-1538.

PROFESSIONAL REGISTRATIONS AND HONORS

President (1997-1998), Vice President (1996-1997) and Board Member (1995-1999) of the Association of Environmental Engineering Professors (AEEP).

Parsons Engineering Science/AEEP Outstanding Doctoral Dissertation Award (1997): Advisor to Dr. Xiaoyan Li

USANC Founders Award (1995) for best paper in Water Research by a US author (Haldane and Logan, 1994)

Fulbright Scholar- 1993 (University of Constance, Germany)

University of California Regents Fellowship 1982 - 1983

Rensselaer Polytechnic Institute Scholarship 1975 - 1979

New York State Regents Scholarship 1975 - 1979

Lewis J. Coonley Award in Chemical Engineering (R.P.I. 1979)

Phi Lambda Upsilon - Chemical Honor Society

PROFESSIONAL MEMBERSHIPS

American Association for the Advancement of Science (AAAS)

American Chemical Society (ACS)

American Society of Civil Engineers (ASCE)

American Society for Limnology and Oceanography (ASLO)

American Society for Microbiology (ASM)

Association of Environmental Engineering Professors (AEEP)

International Association on Water Quality (IAWQ)

Water Environment Federation (WEF)

JACIMARIA RAMOS BATISTA

Assistant Professor, Civil and Environmental Engineering Department
University of Nevada, Las Vegas, 4505 Maryland Parkway, Las Vegas, NV 89154-4015
Phone: 702-895-1585, Email: Jaci@ce.unlv.edu

EDUCATION

1995 Ph.D. Environmental Engineering, The Pennsylvania State University, University Park, PA. GPA 3.6/4.0. Advisors: Dr. James C. Young and Dr. Kwadwo A. Osseo-Asare

1990 M.S. Environmental Engineering, Montana College of Mineral Science and Technology, Butte, Montana, December 1990.

1987 B.S. Mining Engineering, Federal University of Ouro Preto, Ouro Preto, Minas Gerais, Brazil. Rank: 3/83.

PROFESSIONAL POSITIONS AND EXPERIENCE

1997-present Assistant Professor (tenure-track): University of Nevada Las Vegas, Civil and Environmental Engineering Department. Have taught undergraduate and graduate courses in environmental and civil engineering, including Units Operation, Hazardous and Solid Waste Management, Introductory Engineering Design.

1996-1997 Assistant Professor (non-tenure track): The Pennsylvania State University, Civil and Environmental Engineering Department, University Park.

1995-1996 Environmental Consultant: Buchart Horn GmbH, Germany. Performed characterization study of sludge contained in biological oxidation ponds at Incirlik, Turkey. Investigated possible reclamation options for the ponds, provided cost estimate for possible reclamation options, and wrote final report on the study. 1995-1996.

1991, 1992 Environmental Engineer (Summers only). FMC Gold Company, Gabbs, Nevada, USA. Responsibilities included the preparation of the final closure plan for the facility, including screening of technologies for wastewater treatment, testing of ion exchange resins, and running an activated carbon/alumina adsorption pilot plant to remove selenium and metal-cyanide complexes from an industrial wastewater; selection of available technologies to dispose of mine leachate containing cyanide and toxic metals; Conceptualizing and managing a land application project for the disposal of contaminated mine leachate; and the Preparation of a plan and cost estimate to reclaim and revegetate disturbed mine land. Summers 1991/92.

HONORS AND AWARDS

Full Scholarship for Master's Degree. Montana Power Company, Butte, Montana, USA. 1989 to 1990.

Full Scholarship fro Ph.D. Degree. The Pennsylvania State University and CNPQ.

Student Research Award. Water Pollution Control Association of Pennsylvania, Hershey, PA,1993.

PUBLICATIONS

Batista, Jacimaria R.; Doctoral Dissertation. Removal of Aqueous Selenium by Activated Alumina Adsorption: The Influence of Calcium and Aqueous Silica. The Pennsylvania State University, University Park, PA, 1995.

Batista, Jacimaria R.; M.Sc. Thesis. The Use of Diversion Channels for Effluent Quality Control at the Novo Astro Mine. Montana College of Mineral Science and Technology, Butte, Mt, 1990.

Batista, Jacimaria R. and James C. Young. Removal of Selenium from Gold Heap Leachate by Activated Alumina. 1997. *Minerals and Metallurgical Processing, AIME.*(To be published in the May 1997 issue). (Refereed).

Batista, Jacimaria R. and James C. Young. Removal of Soluble Selenium by Activated Alumina Adsorption. Paper presented at the *65th Annual Conference of the Water Pollution Control Association of Pennsylvania.* Hershey, PA, June 13-16, 1993. (Refereed by Abstract).

Batista, Jacimaria R. and James C. Young. The Influence of Aqueous Silica on the Adsorption of Selenium by Activated Alumina. Paper published at the *Proceedings of the 1994 Annual Conference of the American Water Works Association (AWWA)*, New York, NY. June 19-23, 1994. (Refereed by Abstract).

Batista, Jacimaria R. and James C. Young. Adsorption of Selenium From Gold Heap Leachate by Activated Alumina. Final Report. Environmental Resources Research Institute (ERRI), The Pennsylvania State University, PA 16801, USA. June 1993.

STEVE PRICE, P.E.

Environmental Engineer, Camp Dresser & McKee
Professional Civil Engineer: Arizona, 1990; California, 1991

Education

B.S., Civil Engineering, Iowa State University, 1983
M.S., Civil Engineering (Environmental Emphasis), University of Arizona, 1989

Experience

Mr. Price has 12 years of experience primarily focused on drinking water treatment process evaluations, and facilities design. His professional experience includes a wide range of drinking water issues including regulatory compliance evaluations and treatment facilities engineering. He has been involved with several water quality compliance studies, pilot plant studies, surface water and groundwater process design, and construction/implementation projects.

Design and Construction Projects. Mr. Price has been involved in numerous design and construction projects since 1984. These include designs for several groundwater systems in Arizona and surface water treatment facilities for the Santa Clara Valley Water District, City of San Francisco, City of Benicia, and Contra Costa Water District. Prior to joining CDM, he was involved in the design and construction of several steel and prestressed concrete reservoirs, water system pump stations, and wastewater treatment plants. Currently, Mr. Price is managing a multi-million dollar project to convert the residual disinfectant from chlorine to chloramine for the City of San Francisco, CA.

Compliance and Water Quality Studies. Mr. Price has been involved in numerous studies since joining CDM. He was the project manager for an extensive iron corrosion control pilot study for the Tucson, Arizona Water Department. This highly visible project identified a strategy which would allow Tucson to use Colorado River water without the formation of red water in the distribution system. Mr. Price was involved with multi-million dollar pilot studies with the City of San Francisco and Santa Clara Valley Water District to identify long-term needs for these utilities. The ACWD project was completed jointly with other South Bay Aqueduct water users, the Metropolitan Water District of Southern California, and the University of North Carolina. This project was part of an AWWARF project to evaluate bromate mitigation when using advanced oxidation processes.

Along with involvement in numerous pilot studies, Mr. Price has been the project manager or engineer for many water treatment plant evaluations and compliance studies. Mr. Price completed a comprehensive evaluation of East Bay Municipal Utility Districts Upper San Leandro plant. This study provides the groundwork for the District to conduct a self-assessment as part of the Partnership for Safe Water. Specific improvements were recommended to reliably provide a firm treatment capacity at this facility. Mr. Price has also completed studies for the City of Benicia and Metropolitan Water District of Southern California (MWD). The Benicia study evaluated compliance with the current and anticipated Disinfection By-Product (DBP) Rule and the Surface Water Treatment Rule. The MWD project evaluated the standard design criteria and treatment performance for the washwater reclamation processes (WWRP) at filtration plants totaling over

2,000 mgd. Mr. Price also evaluated the WWRP facility at the Los Angeles Aqueduct Filtration Plant.

R. BRUCE CHALMERS, P.E.

Project Manager/Project Engineer, Camp Dresser & McKee
Professional Engineer: California (1983), Nevada

Education

M.S. - Civil Engineering, California State University, Long Beach, 1994
B.S. - Civil Engineering, University of California, Los Angeles, 1980

Experience

Mr. Chalmers has 18 years of design and managerial experience in the fields of water and wastewater engineering. He has been involved in projects encompassing the planning, design and construction management of water storage and distribution facilities; groundwater remediation; sewage collection systems, sewage lift stations, water booster stations, water and wastewater treatment plants, and water storage reservoirs. He has been responsible for the design and management of numerous water and sewer projects, including the design of two reverse osmosis treatment plants, three VOC treatment plants, an ion exchange treatment plant, and two GAC water treatment systems. Mr. Chalmers has extensive field experience with responsibilities as the resident engineer for the construction of a water treatment plant expansion. Mr. Chalmers has also acted as project manager for the construction management of various reservoirs, pipelines and pump stations.

VOC Water Treatment. Mr. Chalmers was the project manager for two VOC water treatment plants with a total capacity of 6,400 gpm. Packed tower aerators were used to remove VOCs from contaminated groundwater. Work included treatment selection, design, and construction services.

Mr. Chalmers was the task leader for a 5,000-gpm VOC treatment plant at an EPA Superfund site in the San Fernando Valley, California. Conceptual design tasks included treatment evaluation and selection, cost estimates and sensitivity analysis. Additional work included a radon investigation and a GAC regeneration study. The design of the treatment facility, included packed towers (PTAs) for VOC removal, vapor phase GAC off-gas treatment, liquid phase GAC potable water polishing, pump station, construction and O&M cost estimates, GAC usage calculations, and WTP design team coordination. Construction services included major equipment purchasing, subcontractor agreements, shop drawing review, and O&M manuals, in association with CDM Engineers & Constructors.

Mr. Chalmers was the project engineer for a 3.0 mgd granular activated carbon (GAC) water treatment system for the City of Redlands, California. Mr. Chalmers' work included preparation of final plans and specifications, cost estimates, and wellhead piping modifications. He was also responsible for construction management during construction of the site facilities and installation of the GAC contactors.

Mr. Chalmers served as the project engineer for the Monrovia TCE Treatment System Feasibility Report for the San Gabriel Basin Water Quality Authority. The report consisted of an evaluation of packed tower aeration, GAC, and modified air stripping techniques for use by the City of Monrovia to remove TCE contamination for existing wells.

As project engineer for the San Gabriel Basin Water Quality Authority, Mr. Chalmers assisted in the development of an alternative treatment handbook that helps water purveyors in the San Gabriel Basin determine which alternative treatment processes could be used to remove various contaminants from their groundwater. The handbook includes information on potential process technologies, detailed process descriptions, evaluation criteria, and treatment capabilities. The manual was designed to be used in the CERCLA process.

Membrane/Ion Exchange Water Treatment. Mr. Chalmers served as the project engineer for: the 3.2 mgd 17th Street Tustin Desalter reverse osmosis treatment plant for the Orange County Water District and City of Tustin; the 6.0 mgd reverse osmosis treatment plant for the Santa Ana Watershed Project Authority (SAWPA) in Riverside, California; the design of a 3-mgd design/build ion exchange project for the Rubidoux Community Services District near Riverside, California; the project engineer for the Chino Basin Desalter No.1 (West) facilities plan; the Alamitos Barrier Feasibility Study using microfiltration/reverse osmosis to treat tertiary wastewater.

CHARLES J. CRUZ

Environmental Engineer, Camp Dresser & McKee

Education

M.S., Civil Engineering - Environmental Engineering and Science, Stanford University, 1991
B.S., Chemical Engineering - Stanford University, 1985

Experience

Mr. Cruz is a chemical engineer with over six years of experience in chemical and environmental engineering, including process engineering, groundwater remediation, and water treatment. He is experienced in treatment and system design, operation and maintenance (O&M), industrial wastewater management, feasibility and treatability studies, and environmental compliance assessments.

Mr. Cruz designed a 5,000 gallon-per-minute (gpm) groundwater treatment plant for a Superfund site remedy in Southern California. The treatment plant was designed to remove volatile organic contaminants from groundwater by packed tower aeration (PTA) and liquid phase carbon adsorption, with vapor phase carbon adsorption used for abatement of the PTA vapor stream. Responsibilities included process, civil and mechanical design, and preparation of construction drawings.

He conducted startup of a groundwater remediation system for an industrial client in Irvine, California. Duties included treatment system O&M and effluent sampling. Mr. Cruz wrote the O&M manual and prepared monthly reports for the regulatory agency.

He designed a groundwater remediation system for an industrial client in Tustin, California. The remediation system was designed to remove organic and inorganic contaminants by oxidation, clarification, and carbon adsorption. Duties included process design, selection of vendor process equipment, and preparation of plant layout, and piping and instrument (P&IDs) drawings.

Mr. Cruz prepared an operations and maintenance (O&M) manual for a Superfund site remedy in Oklahoma. The site remedy included extraction and treatment of contaminated groundwater and hazardous landfill gases. Responsibilities included preparation of procedures and checklists for pre-startup equipment testing, treatment system operation, equipment maintenance, and routine O&M.

Mr. Cruz conducted startup of a 200-gpm groundwater treatment system which utilized steam stripping and carbon adsorption to remove organic contaminants from groundwater.

Responsibilities included computer control system programming, treatment process optimization, and operations support.

Mr. Cruz designed, constructed, and operated five pilot treatment systems to evaluate physiochemical treatment processes including chemical oxidation, steam/air stripping, and carbon adsorption. Duties included coordination of pilot system projects, preparation of O&M manuals, and operator training and supervision.

He provided waste characterization support for closure of six wastewater surface impoundments. Sampled liquids and solids from several depths in each impoundment and coordinated organic and inorganic chemical analysis. Results of the characterization were incorporated into the closure plan for the surface impoundments.

For a U.S. Air Force base in Southern California, Mr. Cruz prepared a workplan for a remedial investigation. The scope of work included installation of one soil boring and four groundwater monitoring wells to further characterize vadose zone and groundwater contamination with trichloroethylene. Duties included preparation of a field sampling plan, a health and safety plan, a quality assurance project plan, and bid specifications.

He also performed field work for a remedial investigation at a U.S. Air Force base in Southern California. The scope of work included installation of seven soil borings and four groundwater monitoring wells to further characterize vadose zone and groundwater contamination with jet fuel. Responsibilities included preparation of sample log sheets and collection of soil and groundwater samples.

Appendix 6.5 CHARACTERISTICS OF (PER)CHLORATE REDUCING MICROORGANISMS

Many strains of CRMs share many attributes with denitrifiers, but have some characteristics that are atypical of anaerobic microorganisms. This may be due (in part) to the fact that the theoretical energy yield of chlorate reduction is not only larger than for nitrate, sulfate or iron, but it is also larger than oxygen (Malmqvist et al. 1991). While this situation does not necessarily translate to more ATP production than for these other EAs, measured yields of 0.6 g-cell/g-acetate are larger than those typical of anaerobic processes and at the upper end (0.4 to 0.6) for aerobes (Grady and Lim 1980). Cell doubling times of 6 hr for CRMs have been measured in my laboratory, and these doubling times are among the highest recorded for anaerobes (Logan et al. 1998).

Early Studies on CRMs. Sodium chlorate was first used by Bryan and coworkers (Bryan and Rohlich 1954, Bryan 1966) as an alternative to dissolved oxygen in a BOD test. They found that chlorate concentrations of <1000 mg l^{-1} did not adversely affect calculated biochemical chlorate demands (BCDs) and that overall growth kinetics of chlorate reducers were only slightly less than those observed for aerobic microorganisms. Although chlorate has the potential to form chlorite, a toxic chemical, batch and continuous culture experiments have shown that the only end product of chlorate reduction is chloride ion, a non-toxic end product (Malmqvist et al. 1991). After the earlier studies of Bryan and coworkers, the use of chlorate as an alternate electron acceptor for the degradation of organic matter was largely ignored except for an older patent by Korenkov et al. (1976). More recent studies of microbial growth on chlorate were conducted by Malmqvist and coworkers (Malmqvist et al. 1991, Malmqvist et al. 1994); these studies suggest the researchers thought that they were the first to show that chlorate could sustain microbial growth (they did not mention the earlier work by Bryan and co-workers).

It appears that chlorate respiring microorganisms (CRMs) are widely distributed in the natural environment, although it is not known if chlorate respiration is actually occurring in any of the environments sampled. Bliven (1996) tested different sources for chloride production from chlorate (500 mg/L) in BOD bottles amended with a glucose and glutamic acid solution (final concentration, 300 mg/L). The concentrations of chloride (mg/L) obtained after eight days of incubation by source was: anaerobic digester, 156; pulp and papermill wastewater, 63; primary clarifier effluent, 57; trickling filter effluent, 55; soil sample, 51. van Ginkel et al. (1995) found chlorate reduction by river (Ijssel) samples, anoxic sediments from a ditch, surface soils (from a public garden), and a waste water treatment plant treating primarily domestic sewage. Microbial reduction of chlorate was supported by several many different organic chemicals, including: carboxylic acids, alcohols (ethanol and propanols), and some amino acids; and inorganic compounds including H_2S and H_2. Oxygen inhibited chlorate reduction, but chlorate was completely converted to chloride in the presence of sulfate, Fe(III) and Mn(IV). Under denitrifying conditions, gas formation but not chloride production was observed implying that nitrate inhibited chlorate respiration (van Ginkel et al. 1995).

Chlorate- and Perchlorate-Respiring Isolates. Differing reports on strain size and morphology, spore formation, and chemicals that serve as reductants make it apparent that the ability to reduce (per)chlorate is not limited to a single bacterial species. It is suspected, although not proven, that isolates capable of perchlorate respiration are also capable of reduction of several other halo-oxygenated compounds such as chlorate. Microbes known to respire both chlorate and perchlorate include: *Vibrio dechloraticans* Cuznesove B-1168 (Korenkov et al. 1976); *Ideonella dechloratans* (Malmqvist et al. 1994); GR-1, a strain identified to belong to the β subgroup of *Proteobacteria* (Rikken et al. 1996); and *Wolinella succinogenes* HAP-1, an obligate anerobe (Wallace et al. 1996). Strains of *Pseudomonas fluorescens* have been found to reduce bromate (Hijnen et al. 1995). One chlorate-respiring isolate, AB-1, identified as most similar to *Comomonas testasteroni* using a Biolog test (as was *I. dechloratans*) was not tested for perchlorate reduction (Bliven 1996) but in all other cases tested, perchlorate reducers also reduced chlorate. All of these chlorate respiring microbes (CRMs) except HAP-1 are facultative anaerobes and are thought to be related to denitrifying organisms; it has been reported, however, that chlorate respiring cultures may lose the ability to reduce nitrate when cultivated on chlorate for long periods (Malmqvist et al. 1994).

Malmqvist and Welander (1992) obtained four chlorate reducing bacterial strains using streak plates and acetate/chlorate agar plates. All four isolates were gram-negative, catalase- and oxidase-positive, motile rods. None of the isolates could use glucose, but Korenkov et al. (1976) indicated growth of their isolate only occurred on glucose in the presence of acetate. They grew aerobically or with nitrate as an electron acceptor. *I. dechloratans* is Gram-negative, motile, rod-shaped (straight or slightly curved, sometimes growing in filaments), and is capable of growth using oxygen or nitrate. It grew on acetate, alanine, asparagine, byutyrate, fructose, glucose, lactate, propionate, pyruvate, and succinate as sole carbon sources, but did not grow on aminobenzoate, phenol and phenylanine. A chlorate respiring isolate was obtained by Bliven (1996), designated AB-1, was a slightly curved rod having a single polar flagellum. It grew aerobically on acetate or anaerobically on acetate and chlorate, but not anaerobically on phenol, benzene, toluene or xylene. Identification of using Biolog microplates indicated a closest similarity to *Comamonas testosteroni* (as was *I. dechloratans*).

The perchlorate-respiring strain, GR-1, isolated by Rikken et al. (1996) was identified as as a Gram-negative, oxidase positive, motile rod. It was isolated from activated sludge on plates containing acetate and sodium perchlorate with incubation under anaerobic conditions. GR-1 grew on acetate, propionate, caprionate, malate, succinate, and lactate, but was unable to grow on glucose, arabinose, mannose, mannitor, N-acetylglucosamine, maltose, gluconate, adipate, and phenyl acetate. GR-1 grew aerobically or on nitrate. It grew on perchlorate in the presence of nitrate, but nitrate decreased measured doubling times from 3 hours to 9 hours. It could also respire on chlorate and Mn(IV), but not using sulphate, iodate, bromate, chlorite, selenate, or Fe(III).

An obligate anaerobic microorganism capable of perchlorate respiration at concentrations of 7 g/L of perchlorate, first designated as HAP-1, and then later classified as *Wolinella succinogenes* HAP-1, was isolated by Wallace et al. (1996) from an anaerobic sewage

enrichment culture using agar plates. It was catalase-negative, with an optimum growth temperature of 40°C (range 20 to 45°C), and grew on H_2 and aspartate, fumarate, and malate, and also on a mixture of H_2 and perchlorate on: pyruvate, succinate, acetate, whey powder, peptone, yeast extract, Brewers yeast, casamino acids, and cottonseed protein. It did not grow on glucose, fructose, galactose, lactose, sucrose, butyrate, citrate, formate, propionate, benzoate, ethanol, methanol, 1-propanol, and starch. Earlier work reported by Attaway and Smith (1993) was conducted using suspended growth reactors that presumably were highly enriched with HAP-1. Aeration was found to inhibit perchlorate reduction, and completely inactived mixed cultures after a 12 hour exposure (Attaway and Smith 1993). The mixed cultures reduced chlorate, nitrate, nitrite, and sulfate. Nitrate or sulfate did not affect reduction; chlorate (10 mM) reduced the rate of reduction, while nitrite and chlorite (10 mM) completely inhibited perchlorate reduction.

Differences and similarities of Denitrifying and (Per)chlorate Reducing Species. Based on the above characteristics of these isolates, there appear to be many common characteristics of these (per)chlorate respiring strains. For all strains (when it was tested), both chlorate and perchlorate could be reduced. Except for *W. succinogenes* (HAP-1), (per)chlorate reduction was partially or completely inhibited by high concentrations of either nitrogen and oxygen, and sulfate could not be used as a terminal electron acceptor. Chlorate-reductase has been isolated from microorganisms that also possess nitrate reductase, implying that chlorate-respiring strains may share many of the attributes of denitrifiers. While it may be that most (per)chlorate strains are facultative anaerobes that are denitrifiers, not all denitrifiers are chlorate reducers. There is also a variable effect of nitrate on (per)chlorate reduction that is interesting. The only exception to the inhibitory effect of nitrate on perchlorate reduction was reported by Attaway and Smith (1993); in their mixed cultures (presumably containing *W. succinogenes* HAP-1), perchlorate was reduced in the presence of nitrate. Although the facultative anaerobe (GR-1) isolated by Rikken et al. (1996) was also able to reduce perchlorate in the presence of nitrate, cell doubling times decreased in the presence of nitrate implying an inhibitory effect of nitrate on perchlorate respiration.

Little is known about the biochemical pathways involved in bacterial utilization of chlorate or perchlorate as an electron acceptor. Although chlorate reductases have been isolated, these enzymes have been obtained from denitrifying strains known to reduce, but not necessarily shown to respire, chlorate. For example, electron transport to oxygen for *Proteus mirabilis* represses formation of nitrate reductase A (NR-A), but in the absence of oxygen and presence of nitrate, NR-A was de-repressed (Oltmann et al. 1976). While the presence of nitrate in turn has been found to repress the expression of chlorate reductase-C (CR-C) in *P. mirabilis*, CR-C is otherwise constitutive even in the presence of oxygen, although it is present at lower per cell activities (DeGroot and Stouthamer 1969). If these enzymes were involved in chlorate respiration, then this suggests that in order for cells to respire using chlorate, both nitrate and oxygen would have to be absent, an observation which is not true for all chlorate respiring strains. In batch cultures, the presence of oxygen may not be detrimental to cell growth for all species examined except HAP-1; because these chlorate reducing isolates have been shown to be facultative aerobes, as long as NO_3^- is absent, dissolved oxygen would be removed by cell growth prior to growth supported by chlorate respiration.

There are important differences in the physiology and biochemistry of denitrifying and perchlorate reducing species. Denitrification does not progress from NO_3^- to N_2 in one step, but rather follows the sequence of: NO_3 6NO_2 6 NO 6 N_2O 6 N_2. Thus, overall it is a five-electron transfer process. In contrast, the conversion of chlorine in perchlorate (Cl^{+7}) to chloride (Cl^-) requires the overall transfer of eight electrons-- and it can be accomplished completely by one bacterium without the detection of toxic intermediates in solution (such as chlorite). The reason for this in at least one strain was determined by Van Ginkel et al. (1996). They were able to isolate a novel enzyme (chlorite dismutase, from strain GR-1) capable of conversion of chlorite (ClO_2^-) to oxygen. This implies a sequence of perchlorate reduction of ClO_4^-66 ClO_2^-6O_2+Cl^-, where the multiple arrows indicate the potential for intermediates such as ClO_3^-. [Recall that GR-1 was a facultative anaerobe capable of reducing a variety of compounds including chlorate, nitrate, and Mn(IV)]. Oxygen produced from chlorite was not found to accumulate in solution, and therefore oxygen was probably used by GR-1 as an electron acceptor. It is not yet known if chlorite dismutase is present in other strains of chlorate and perchlorate microorganisms. GR-1 is the only facultative anaerobce that can continue to reduce chlorate in the presence of nitrate, suggesting that other strains may not necessarily contain chlorite dismutase.

Perchlorate reduction is significantly different from nitrate in that perchlorate is extremely stable in water. Many inorganic chemists use perchlorate under highly reducing conditions in order to maintain ionic strengths while studying the reduction of more easily reduced compounds (Espenson 1997). Perchlorate should, from a thermodynamic perspective, react with many metal complexes but in fact it is stable with almost all complexes except methyl rhenium dioxide suspensions at low pH (where it has very high reaction kinetics) (Espenson 1997). In contrast, nitrate is quite reactive. For example, nitrate was found to be completely reduced by granular metallic iron and hydrogen with a palladium catalyst (with nitrite as an intermediate) within 14 minutes (Siantar et al. 1996). However, both chlorate and perchlorate are stable in water in the presence of zero-valent iron (unpublished data).

Influence of co-contaminants on Treatment Efficiency. We have previously investigated the potential of using (per)chlorate respiring microbes for degradation of persistent chemicals such as benzene, toluene, and xylene. We were unable to obtain cultures that could oxidize these chemicals while reducing perchlorate. However, we did find that phenol could serve as the sole substrate for growth of mixed cultures under chlorate reducing conditions (Logan et al. 1998). Both anaerobic and aerobic pathways are known for phenol degradation. Under denitrifying conditions, phosphate is added to phenol and then carboxylation of phenylphosphate occurs by phenol carboxylase to produce 4-hydroxybenzoate. Since CRMs may have had access to low concentrations of oxygen in chemostat work it is possible that microaerophilic processes may be may be necessary for pollutant degradation. Mono and dioxygenases are important in a number of aromatic compound degradation pathways. Phenol degradation under aerobic conditions by *Pseudomonas putida* occurs by oxygen insertion into the ring leading to ring cleavage and mineralization of phenol. The work by van Ginkel et al. (1996) demonstrating that oxygen is produced by chlorite dismutase, suggests that oxygen could be available for oxygenases to use for ring cleavage.

There is great potential for the degradation of chlorinated aliphatics in mixed cultures under hydrogen oxidizing conditions for two reasons. First, a bacterium has been isolated that is capable of reductively dechlorinating tetrachloroethylene (PCE) to ethylene when grown with H_2 (Maymo-Gatell et al. 1997). It may be possible to bioaugment perchlorate-respiring cultures and biofilms with these microbes in order to facilitate reductive dechlorination of some chemicals. Second, many other chemicals can be reduced under methanogenic conditions (Ballapragada et al. 1997). Although we will not intentionally try to develop a methanogenic consortium, some growth of methanogens is likely in hydrogen fed reactors. The growth of these cells might be sufficient to degrade chlorinated chemicals in the water.

APPENDIX 6.6

DIONEX

Application Note 121

Analysis of Low Concentrations of Perchlorate in Drinking Water and Ground Water by Ion Chromatography

INTRODUCTION

Perchlorate (as ammonium perchlorate), which is widely used in solid rocket propellants, has recently been found in drinking water wells in areas where aerospace materials and munitions have been manufactured and tested.[1] Perchlorate is a health concern, as it interferes with the production of thyroid hormones. Current data suggest that an exposure level range of 4 to 18 µg/L (ppb) is acceptable.[2] Although perchlorate is not yet regulated in the U.S. under the Federal Safe Drinking Water Act, the State of California requires remedial action for drinking water sources containing greater than 18 µg/L of perchlorate.

This Application Note details a new method developed to quantify low levels of perchlorate. A large loop injection (1000 µL) is used with an IonPac® AS11 column and suppressed conductivity detection to quantify perchlorate in drinking water down to approximately 2.5 µg/L.

EQUIPMENT

Dionex DX-500 Ion Chromatography system consisting of:
- GP40 Gradient Pump
- CD20 Conductivity Detector
- AS40 Automated Sampler
- LC20 Chromatography Enclosure with a rear-loading valve

4-L Plastic bottle assemblies (two for external water mode)

PeakNet Chromatography Workstation

REAGENTS AND STANDARDS

Deionized water (DI H_2O), Type I reagent grade, 18 MΩ-cm resistance or better

Sodium hydroxide, 50% (w/w) aqueous solution (Fisher Scientific or other)

Sodium perchlorate, 99% ACS reagent grade or better (Aldrich or other)

Potassium sulfate, 1000 mg/L aqueous solution (Ultra Scientific or other)

CONDITIONS

Columns:	IonPac AS11 Analytical, 4 x 250 mm (P/N 44076) IonPac AG11 Guard, 4 x 50 mm (P/N 44078)
Eluent:	100 mM Sodium hydroxide
Run Time:	12 min
Flow Rate:	1.0 mL/min
Sample Volume:	1000 µL
Detection:	Suppressed conductivity, ASRS® (4 mm), AutoSuppression® external water mode
System Backpressure:	600–900 psi (3.95–5.93 MPa)
Background Conductance:	2–5 µS

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solution

Stock perchlorate standard solution (1000 mg/L)

Dissolve 1.231 g of sodium perchlorate in 1000 mL of deionized water to prepare a 1000 mg/L standard. Standard is stable for at least one month when stored at 4 °C.

Working Standard Solutions

Dilute 1000 mg/L standard solution as required with deionized water to prepare the appropriate working standards.

Eluent Solution

100.0 mM Sodium hydroxide

Weigh 992.0 g of deionized water into an eluent bottle. Degas water for approximately 5 minutes. Carefully add 8.0 g of 50% sodium hydroxide directly to the bottle. Mix then quickly transfer the eluent bottle to the instrument and pressurize the bottle with helium at 8 psi (0.055 MPa).

RESULTS AND DISCUSSION

For the best perfomance at low-ppb levels, it is critical that baseline noise be kept to a minimum. To minimize baseline noise, it is necessary to use the ASRS in external water mode rather than the recycle mode. An equilibrated system will produce a background conductance between 2–5 µS. Peak-to-peak noise is typically 10 nS and system backpressure is 600–900 psi (3.95–5.93 MPa). A system blank is determined by using deionized water as a sample. This blank establishes the baseline and confirms the lack of contamination in the system. The linear concentration range was determined to ensure accurate quantification of perchlorate in the 2.5–100 µg/L range. Figure 1 shows the results of a linearity study.

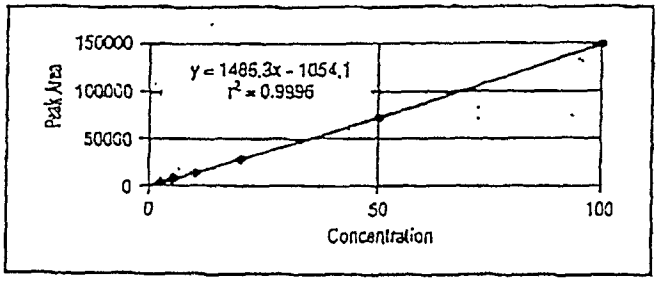

Figure 1 Perchlorate calibration

This plot demonstrates that calibration of perchlorate is linear in the low-ppb range. Figure 2 shows a typical chromatogram of a 20 µg/L perchlorate standard. To determine the method detection limit (MDL), seven injections of the 2.5 µg/L perchlorate standard were made. Table 1 shows the results of a method detection limit study. The 1000 µL injection is large enough to achieve the desired detection limit without overloading the column. Note that this method is not intended for use with high (ppm) levels of perchlorate. The calculated MDL equals 254 ng/L (ppt).

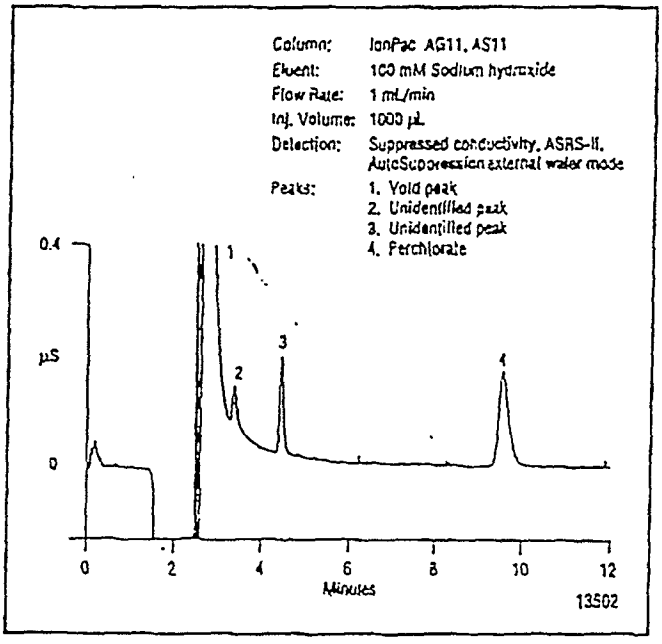

Figure 2 20 µg/L Perchlorate standard

Table 1 MDL for perchlorate based on a 1000 µL injection volume

Injection #	Area counts	Retention time (min)
1	3391	9.48
2	3405	9.57
3	3504	9.50
4	3503	9.45
5	3435	9.47
6	3301	9.52
7	3315	9.43
Average	3408	9.49
SD	81	0.05
RSD	2.38	0.49

MDL=254 ng/L (ppt). MDL=SD$t_{(n)}$ where $t_{(n)}$=3.14 for n=7

Figures 3 through 5 show chromatograms obtained for 2.5 µg/L perchlorate in three different matrices. Figure 3 shows the chromatogram of 2.5 µg/L perchlorate in deionized water. Figure 4 shows 2.5 µg/L perchlorate in tap water. Note that all other anions present in tap water elute in the void volume and do not interfere with perchlorate determination. Some environmental samples may contain low levels of perchlorate in the presence of a large amount of sulfate. Figure 5 shows the determination of 2.5 µg/L perchlorate in the presence of 700 mg/L sulfate. The high concentration of sulfate does not affect perchlorate recovery or the detection limit.

SUMMARY

The method outlined in this Application Note allows the determination of low-µg/L (ppb) levels of perchlorate. Linear concentration ranges have been established to accurately quantify perchlorate in drinking water and ground water samples.

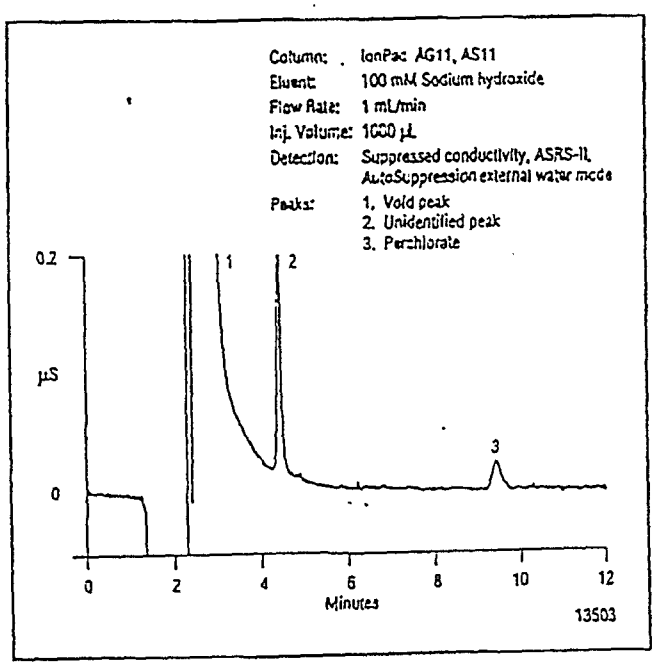

Figure 3 2.5 µg/L Perchlorate standard

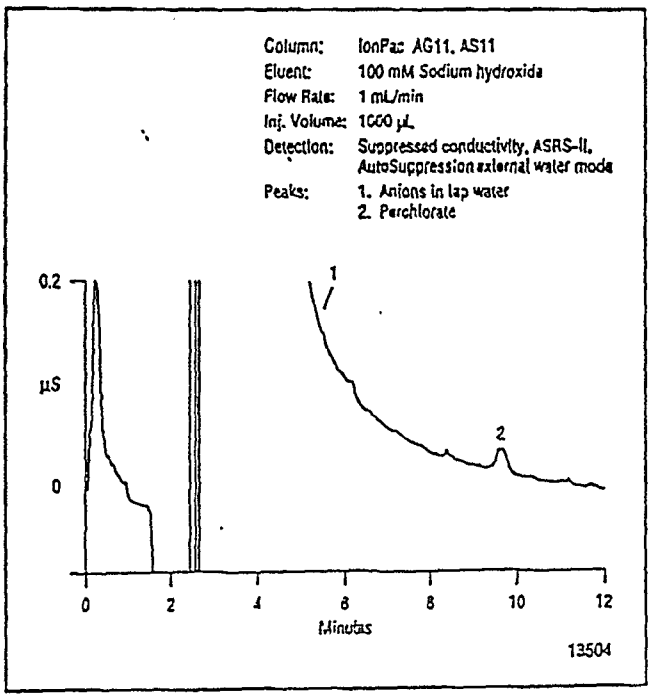

Figure 4 2.5 µg/L Perchlorate in tap water

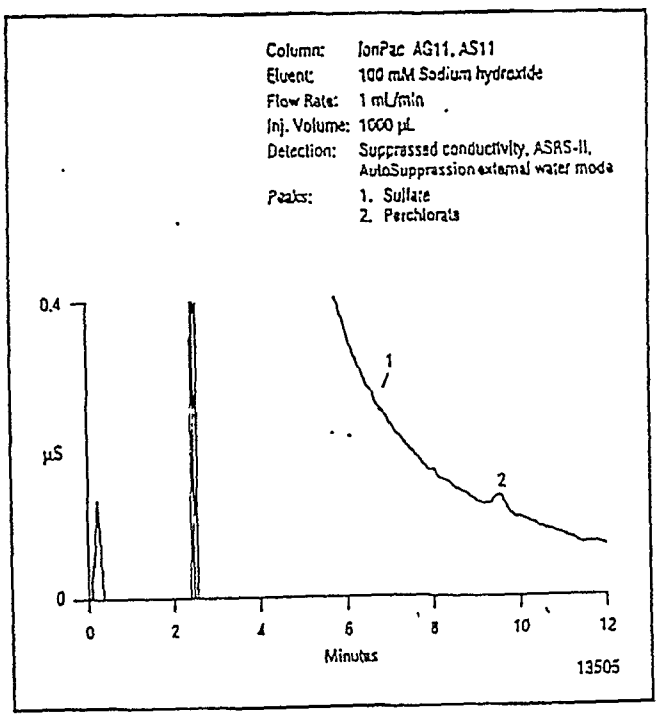

Figure 5 2.5 µg/L Perchlorate and 700 mg/L Sulfate

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2. Correspondence from Joan S. Dollarhide, National Center for Environmental Assessment, Office of Research and Development, to Mike Girrard, Chairman, Perchlorate Study Group, U.S. EPA, 1995.

LIST OF SUPPLIERS

Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, P.O. Box 355, Milwaukee, Wisconsin, 53233, USA. Tel: 1-800-558-9160.

Fisher Scientific, 711 Forbes Ave., Pittsburgh, Pennsylvania, 15219-4785, USA. Tel: 1-800-766-7000.

Ultra Scientific, 250 Smith Street, North Kingstown, Rhode Island, 02852, USA. Tel: 401-294-9400.

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